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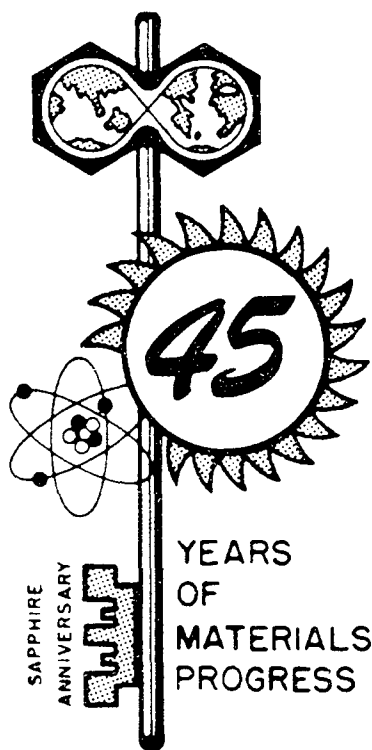


## PHOSPHINOBORINE POLYMERS

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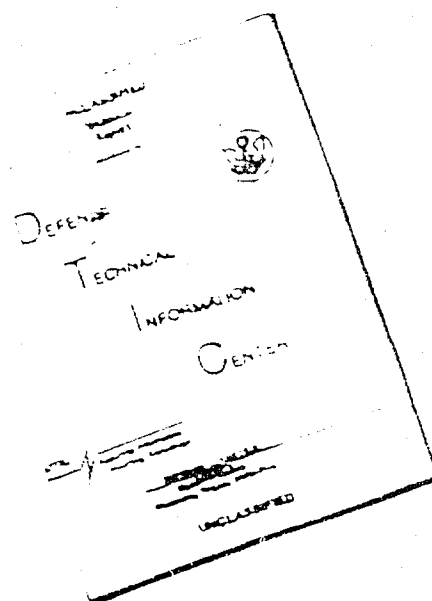
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by the American Potash & Chemical Corporation, Whittier, California  
Dr. Ross I. Wagner and Robert M. Washburn  
and  
University of Southern California, Los Angeles, California  
Dr. Anton B. Burg)

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**Abstract:**

B-P Polymers: A series of new linear poly-P-methyl-n-alkyl-borophanes were prepared and evidence suggests depolymerization of these materials proceeds by loss of monomer units at the chain ends. A number of new P-substituted triborophane derivatives were prepared as well as several partially B-halogenated derivatives of P-hexamethyltriborophane. New Approaches to Thermally Stable Polymers: A number of diarylphosphonyl azides,  $\text{Ar}_2\text{P}(\text{O})\text{N}_3$ , were prepared and characterized. The azides react with trivalent P compounds to yield phosphoranes. Inorganic Polymer Components: New IR spectra of  $(\text{R}_2\text{PBH}_2)_3$  compounds have structural implications bearing upon the theory of their stability. IR spectra also confirm the structure  $(\text{CF}_3\text{HP}(\text{O})(\text{OH})_2)_n$ , relating to the question of the stability of possible polymers having phosphinic-anhydride connections. Trifluormethyl acetoxyphosphines offer a route to P-O-P bonding and to  $(\text{CF}_3\text{PO})_n$  polymers. (Author)

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**Annotation:**

DEVELOPMENT OF B AND P COMPOUNDS AND POLYMERS FOR USE AS ELASTOMERS, ADHESIVES AND FOR FLUIDS HAVING EXTREME CHEMICAL AND THERMAL STABILITY. INCLUDED IS RESEARCH ON BOROPHANES, BORINES, PHOSPHONYL AZIDES, PHOSPHORANES AND PHOSPHINES.

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## FOREWORD

This report was prepared by Dr. Ross I. Wagner and Mr. Robert M. Washburn, American Potash & Chemical Corporation, Research Department, Whittier, California, and Dr. Anton B. Burg, University of Southern California, Los Angeles, California, under USAF Contract No. AF 33(616)-7810. This contract was initiated under Project No. 1(8-7340), "Nonmetallic & Composite Materials," Task No. 73404, "New Chemicals & Methods." The report was administered under the direction of Directorate of Materials and Processes, Deputy Commander/Technology, Aeronautical Systems Division, with Lt. W. K. Musker and Dr. W. L. Lehn acting as project engineers.

This report covers work conducted from January 1961 through December 1961.

The work at American Potash & Chemical Corporation Laboratories was carried out under the direction of Dr. D. R. Stern, Manager, Research, Dr. K. R. Eilar, Assistant Manager, Research, and Head, Organic Chemistry Section, and Dr. Ross I. Wagner who acted as project leader. Boron-Phosphorus Polymers work was performed by Messrs. Earl M. Evleth, Marvin H. Goodrow, Stanley E. Gordon, Howard N. Hammar, Francis X. Maggio, Harley J. Rockoff, and Charles O. Wilson, Jr. New Approaches to Thermally Stable Polymers were carried out by Messrs. Roger A. Baldwin and Franklin A. Billig under the direction of Robert M. Washburn.

The work at the University of Southern California was carried out under the direction of Dr. Anton B. Burg under Subcontract No. AF 6913-1 and is reported in Appendix I. Dr. Burg was assisted by Messrs. Hans W. Birnkraut, John F. Nixon, and Louis K. Peterson.



## ABSTRACT

Boron-Phosphorus Polymers. A glass cloth laminate was prepared with the resin, poly-methylsesquimethyleneborophane, but it had too low a heat distortion temperature for high temperature applications. Other related resin systems have been studied briefly. A series of new linear poly-P-methyl-n-alkyl-borophanes were prepared and further evidence was obtained suggesting that depolymerization of these materials proceeds by loss of monomer units at the chain ends. A number of new P-substituted triborophane derivatives were prepared as well as several partially B-halogenated derivatives of P-hexamethyltriborophane. A simple synthetic procedure has been developed to convert these partially B-halogenated compounds into P-hexamethyltriborophane derivatives carrying a variety of B-substituted functional groups.

New Approaches to Thermally Stable Polymers. A number of diarylphosphonyl azides,  $\text{Ar}_2\text{P}(\text{O})\text{N}_3$ , have been prepared and characterized. The azides react with trivalent phosphorus compounds to yield phosphoranes,  $\text{Ar}_2\text{P}(\text{O})\text{N}=\text{PR}_3$ , having excellent hydrolytic, oxidative, and thermal stability.

Inorganic Polymer Components. The general purpose of discovering new chemistry of polyvalent light elements has been pursued further with some emphasis upon the understanding of molecular patterns relevant to polymer situations. New infrared spectra of  $(\text{R}_2\text{PBH}_2)_3$  compounds have structural implications bearing upon the theory of their stability. Infrared spectra also confirm the structure  $(\text{CF}_3\text{HPOOH})_2$ , relating to the question of the stability of possible polymers having phosphinic-anhydride connections. Trifluoromethyl-acetoxyphosphines offer a route to P-O-P bonding and to  $(\text{CF}_3\text{PO})_n$  polymers. Such oxyphosphines suggest connecting links for macromolecular fluorocarbons. The basic depolymerization of  $(\text{CF}_3\text{P})_n$  was studied further, and relates to the problem of managing inorganic monomers for controlled polymerization. The relation of  $\text{P}_n$  chain-length to stability in open-chain polyphosphines also is emerging from the study of the new compounds  $\text{P}_3(\text{CF}_3)_5$  and  $\text{H}_2(\text{CF}_3\text{P})_4$ . A new area of resin chemistry may emerge from the complex reaction of  $(\text{CF}_3)_2\text{PCN}$  with  $\text{B}_2\text{H}_6$ , and the probable  $\text{CF}_3\text{P}(\text{CN})_2$  relates to the same purpose.

## PUBLICATION REVIEW

This technical documentary report has been reviewed and is approved.

FOR THE COMMANDER:

*William E. Gibbs*

William E. Gibbs  
Acting Chief, Polymer Branch  
Nonmetallic Materials Laboratory  
Directorate of Materials and Processes



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## I. INTRODUCTION

The primary objective of this program is research in the field of borophane compounds leading toward the synthesis of polymeric materials which are basically inorganic in nature and are capable of development into elastomers, adhesives and/or fluids having extreme chemical and thermal stability. Also under investigation are a number of screening reactions which should lead to new thermally stable polymers involving P-N, B-N, and Si-O-C<sup>O</sup> bonding systems.

The borophanes offer a promising field of study since as a class these compounds are unusually resistant to thermal decomposition and to oxidative and hydrolytic attack.

The two basic approaches to the problem of preparing useful borophane compounds are: (1) altering the substituents on the boron and phosphorus atoms, and (2) changing the degree of polymerization. The changes in physical or chemical properties resulting from varying substituents or changing degree of polymerization are compared with the properties of P-hexamethyltriborophane,  $[(CH_3)_2PBH_2]_3$ , as the reference standard.

Efforts directed toward discovering stable new polymer bonding systems have produced borimidazole (B-N), carboxy-silanol (SiOC<sup>O</sup>), and phosphonimido-phosphorane ( $\overset{O}{\parallel}PN=P\equiv$ ) compounds as well as the interesting phosphonyl azide intermediates used for the latter system.

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## II. BORON-PHOSPHORUS POLYMER GLASS CLOTH REINFORCED LAMINATES

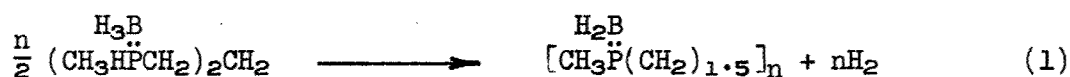
### A. Discussion

Three borophane resin systems have been investigated in varying degree as candidate laminating resins. The first of these resins, poly-P-methylsesquimethyleneborophane, which is derived from 1,3-trimethylene-P,P'-bis(methylphosphine borine), was the most thoroughly studied. A considerable amount of information on preparation and handling of borophane laminating resins was derived from this study although the resin itself proved to retain a certain amount of thermoplastic character which made it unsuitable for the intended application. The second resin was derived from the reaction product of methyl-β-hydroxyethylphosphine and diborane. This material was investigated only briefly since it appeared to have poor oxidative and hydrolytic stability. Investigation of the resin formed on pyrolysis of methylphosphine borine has just begun and proper conditions for preparation of a useful prepolymer have not yet been determined.

#### 1. P-Methylsesquimethyleneborophane Polymer

##### a. Preparation of Laminates

Attempts to polymerize 1,3-trimethylene-P,P'-bis(methylphosphine borine) (equation 1) directly in a glass cloth laminate in the hydraulic press failed, due to volatilization of the adduct at the temperature (200°C.) necessary for a reasonable rate of polymerization. Results of these experiments are listed in Table I.



A number of experiments were run to determine the optimum degree of prepolymerization required for effective use of the prepolymer in laminates containing approximately 30% resin by weight. During the pressing operation the prepolymer must have good flow characteristics but still the resin loss must be minimized. Table II lists some properties of the resin at varying degrees of polymerization. In Figure 1, the evolution of hydrogen from 1,3-trimethylene-P,P'-bis(methylphosphine borine) is plotted as a function of time at 202°C. (equation 1). After 12 hrs. the resin is so highly cross-linked that it could only be applied to the cloth as a powdered solid and did not have enough flow at 260°C. to completely cover the glass cloth. The same situation obtains for the 6-hr. resin although slightly better results were observed if the prepolymer were applied as a gel coat.

The best results obtained so far have been with a 5-hr. prepolymer which at room temperature is an extremely brittle colorless crystalline solid easily ground to a powder. The softening point of the 5-hr. prepolymer was determined to be 92-103°C. on a Fisher-Johns melting point



TABLE I

Attempts to Prepare Laminates by Direct Pyrolysis of  
1,3-Trimethylene-P,P'-bis(methylphosphine borine)

Expt. No.	Resin Content, %		Differential Resin Loss, %	Curing Cycle		
	Before Pressing	After Pressing		Time, hrs.	Temp., °C.	Ram Force, tons
1151-3A	44.0	13.3	30.7	0.75	204	0
1151-3B	44.0	9.5	34.5	0.75	204	0
1151-4	44.0	14.0	30.0	0.75	204	0
1151-5B	14.5	4.3	10.2	0.75	204	0



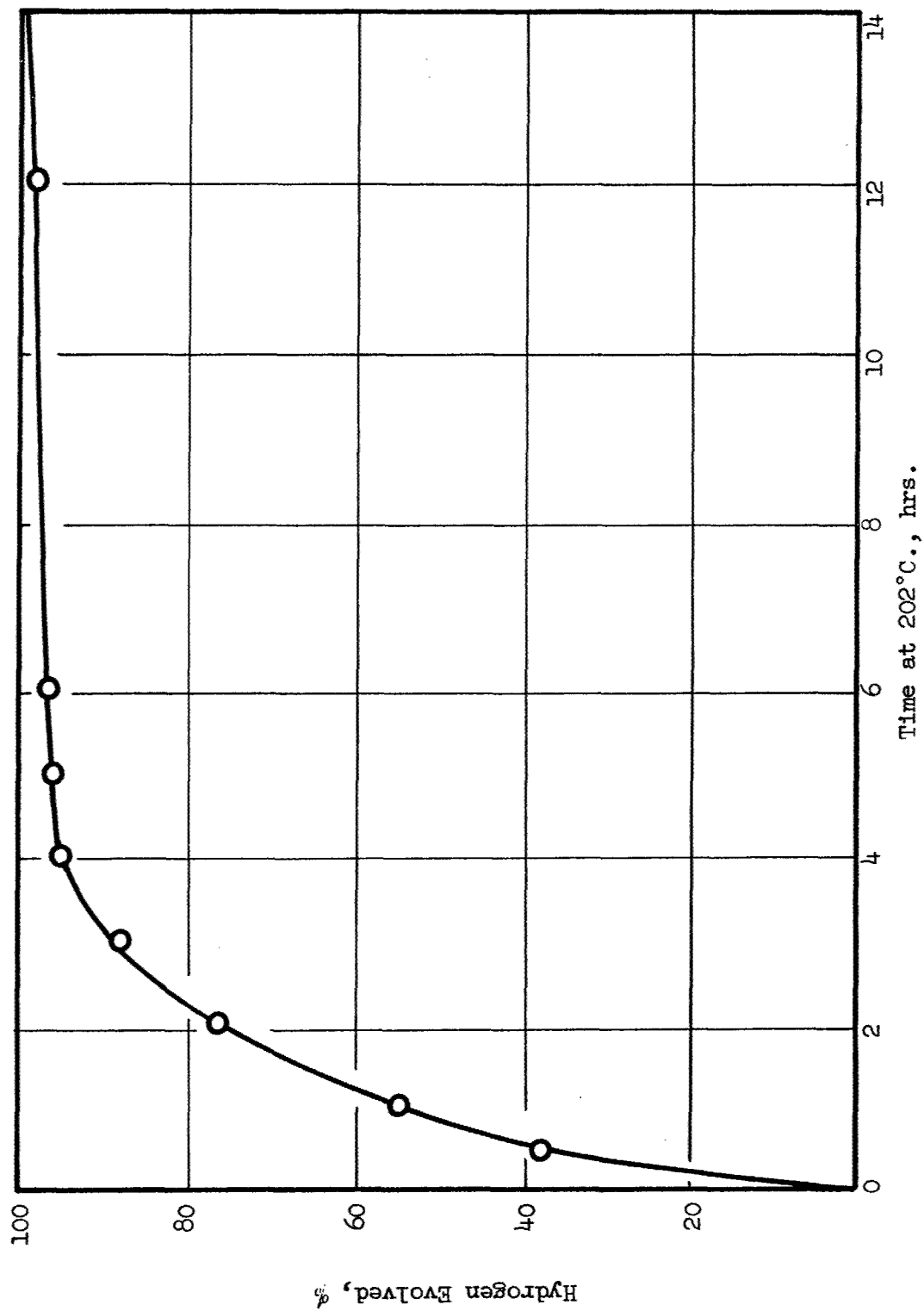


FIGURE 1. Prepolymerization of 1,3-Trimethylene-P,P'-bis(methylphosphine borine)



TABLE II

Some Properties of Prepolymerized 1,3-Trimethylene-  
P,P'-bis(methylphosphine borine)

Expt. No.	Time at 202°C., Hrs.	H <sub>2</sub> Evolved, % of Theor.	Softening Point, °C.	Solubility in Toluene
1391-66	0.5	37.8	-	-
1391-66	1.0	54.9	-	-
1391-66	2.0	76.3	-	-
1151-9	3.0	88	55-65	Sol.
1151-15	4.0	95	64-75	Sol.
1391-66	4.0	95.2	-	-
1151-24	5.0	96	92-103	Sol.
1151-20	6.0	97	98-112	Insol. (gel in di- lute sol.)
1151-16	12.0	98	142-191	Insol.
1391-66	12.0	98.3	-	-



apparatus, and the solubility was great enough to prepare solutions of 50% solids concentration in toluene for application to the glass cloth. The solutions facilitate impregnation of the glass cloth with this resin which has low loss during the laminating operation. In Table III are listed the data pertaining to glass cloth reinforced methylsesquimethyleneborophane polymer laminates prepared from the resin with varying degrees of prepolymerization.

After several months' storage of the adduct under argon at ambient temperature, the 5-hr. prepolymer prepared from it was no longer sufficiently soluble in toluene, and the softening point raised to 112-118°C. Laminates produced from this prepolymer were soft, peeled apart easily, and had a tendency to ignite at the laminating temperature of 260°C. Infrared analysis of the adduct showed an absorption band not present in the spectrum of the original adduct at  $3.22\mu$  attributed<sup>1</sup> to OH on boron suggesting some oxidation as a result of frequent sampling. Purification of the partially oxidized adduct was accomplished by washing with water. A 5-hr. prepolymer prepared from the purified adduct was a clear, crystalline solid with a softening point of 87-92°C. Toluene solutions of the prepolymer at 40-50% solids concentrations were soft gels rather than true solutions. These differences in properties in no way effected the formation of laminates from this material. No ignition of vapors at the laminating temperature (260°C.) was observed. A good 3.5 x 4 in. laminate with a density of 1.69 g./cc. containing 28.5% resin was formed from this purified prepolymer.

All laminates pressed in air had a strong odor of phosphine suggesting, perhaps, some oxidative degradation had occurred during the laminating process. A platen designed to permit gas to enter the area enclosed by 1/16-in. spacers was made and laminates were produced from the 5-hr. prepolymer under a continuous stream of argon. These laminates had comparatively little odor but the resin loss during the laminating process was higher (Expt. No. 1151-30; 33, Table III) suggesting that the odoriferous products may have been more volatile polymer fractions which were swept out in the gas stream, or more probably that the retained resin did not gain weight due to air oxidation.

#### b. Density of the Laminate

Reliable values for the heat distortion temperature of resins is dependent on obtaining a void-free test specimen. Determination of the resin content of a borophane laminate cannot be made by burning away the resin because of the high ash content. Accordingly, a measurement of the density of the laminate and comparison with the theoretical density of a laminate of given dimensions and glass content seemed to be a simple method of determining resin content and void volume of the laminates.

The density of poly-P-methylsesquimethyleneborophane resin was determined to be 1.04 g./cc. by flotation in chlorobenzene and that of the glass to be 2.56 g./cc.\* using an air comparison pycnometer (Beckman No. 930). Using

\*United Merchants Industrial Fabrics, the manufacturer of Type 181 glass cloth, gives 2.55 g./cc. for the glass density.



TABLE III

Preparation of Glass Cloth Reinforced Methylsesquimethylene-  
borophane Polymer Laminates from Prepolymerized 1,3-Trimethylene-  
P,P'-bis(methylphosphine borine)

Expt. No.	Resin Content, %		Differential Resin Loss, %	Prepolymer- ization time, hrs.	Curing Cycle		
	Before Pressing	After Pressing			Time, hrs.	Temp., °C.	Ram Force, Tons
1151-5A	14.5	14.1	0.4	2.5	0.75	204	0
1151-6	14.2	14.0	0.2	2.5	2.0	204	0
1151-7	24.7	22.0	2.7	2.5	0.5 0.5	204 204	0 5
1151-11	-	23.8	-	3.0	0.5 0.5	204 260	0 5
1151-12	-	24.0	-	3.0	1.0	260	5
1151-14	42.2	30.6	11.6	3.0	0.25 0.75 0.66	204 260 260	0 1 5
1151-18	40.0	12.7	27.3	4.0	1.0 2.25	204 260	0 7
1151-19	38.5	30.1	8.4	4.0	1.0 2.5	204 260	6 6
1151-21A	38.2	32.2	6.0	6.0	1.0	260	6
1151-21B	31.9	30.7	1.2	6.0	1.0	260	6
1151-25	33.3	29.8	3.5	5.0	0.25 1.0	260 260	0 6
1151-26	32.4	30.2	2.2	5.0	0.25 1.0	260 260	0 6
1151-28	40.3	36.4	3.9	5.0	0.25 1.0	260 260	0-2 6
1151-30*	36.0	30.6	5.4	5.0	1.0	260	6
1151-33*	29.0	22.2	6.8	5.0	0.25 1.0	149 260	0 6
1151-41	33.2	29.2	4.0	5.0	1.0	260	6



these data the theoretical density (1.70 g./cc.) and resin content (34.4%) were calculated for a 1/16 in., 6-ply laminate.

c. Heat Distortion Temperature

The standard ASTM test D648-56<sup>2</sup> for "Heat Deformation of Plastics Under Constant Load" (264 psi) was not applicable to the glass reinforced laminates. In attempted calibration experiments the heat distortion temperatures of laminates prepared from standard epoxy formulations were not observed at approximately 100°C. above the maximum useful temperature for the formula. Some charring and degradation were observed before a deflection reading could be obtained. Since a solid unreinforced sample of P-methylsesquimethyleneborophane could not be cast readily because hydrogen evolved during the cross-linking process, modification of the test was necessary to compensate for the obvious reinforcing effect of the glass cloth. The heat distortion temperatures of the unreinforced standard epoxy formulations were determined using the standard ASTM test under a load of 264 psi and then the loading was increased so that the corresponding laminates showed the identical heat distortion temperature. Using this increased load the heat distortion temperature of the P-methylsesquimethyleneborophane laminate was measured as 60°C.

Each of the two epoxy formulations has a heat distortion temperature just below the maximum usable temperature (thermal stability limit), e.g., HDT 106°C. and maximum temperature 116°C.<sup>3</sup> for samples 70-1 and 70-2 and HDT 142°C. and maximum temperature 149°C.,<sup>3</sup> for sample 71 (see Table IV). The large difference between the HDT 60°C. and the maximum temperature > 260°C. for P-methylsesquimethyleneborophane suggests that this resin is somewhat thermoplastic. The borophane resin test specimen showed no permanent damage so that glass adhesion appears not to be an important factor contributing to the low HDT value.

d. Thermal Stability of Poly-P-methylsesquimethyleneborophane

During formation of laminates little or no evidence of decomposition of the polymer was observed at 260°C. but raising the temperature to 280°C. in an attempt to reduce the press time resulted in considerable oxidation of the polymer. The spontaneous ignition temperature in air for poly-P-methylsesquimethyleneborophane was previously determined to be 312°C.<sup>4</sup>.

To determine the thermal stability in the absence of air, a sample of polymer, which had been polymerized at 202°C. for 12 hrs., was sealed in an evacuated glass tube and heated at 320°C. for 1 hr. after which time it had changed to a viscous semi-solid. These data suggest that a practicable utilization temperature would be in the range 260-280°C.



TABLE IV

Heat Distortion Temperature Comparisons

Unreinforced Resin			12-Ply Type 181 Glass Cloth Reinforced Resin	
Sample No.	Stress, psi	HDT, °C.	Stress, psi	HDT, °C.
70-1	264	142	1,377	142
70-2	264	142	1,377	140
71	264	106	1,377	108
86	--	--	1,377	60



## 2. Resin from Methyl- $\beta$ -hydroxyethylphosphine and Diborane

### a. Preparation of the Borine Adduct of Methyl- $\beta$ -hydroxyethylphosphine

For the purpose of obtaining a borophane polymer with reactive functional groups for further cross-linking and possibly improved adhesion to glass, an attempt was made to prepare the borine adduct of methyl- $\beta$ -hydroxyethylphosphine according to Equation (2).



Alternatively, the reaction may proceed to form the borate ester according to Equation (3).



In mixing the reagents hydrogen was evolved equal to 72% of the theoretical based on Equation (3). Infrared analysis of the product showed a mixture of both tri- and tetracoordinate borate ester functions as well as the absorption bands associated with O-H, B-H and P-H bonds. The adduct mixture underwent polymerization at 180°C. during 2 hrs. to form a white solid which had a softening point of 90-100°C. and which was soluble only in ethanol possibly with some reaction.

### b. Preparation of Laminates

A 6-ply Type 181 glass cloth laminate was formed successfully at 260°C. using an ethanol solution of the prepolymer and the laminating techniques described for sesquimethyleneborophane polymers. The results are listed in Table V. A continuous stream of argon was used during the laminating procedure because the methyl- $\beta$ -hydroxyethylphosphine borine adduct exhibited a marked sensitivity to oxidation.

This sensitivity may possibly be attributed to the presence of B-O-C bonds. The laminate was brittle at room temperature and remained rigid at 110°C. However, 40 min. immersion at room temperature in distilled water caused complete delamination.

Attempts to laminate by using the polymerized adduct directly failed, due to excessive volatilization at the press temperature (260°C.).

## 3. Methylborophane Polymers

Two attempts to form a soluble prepolymer from methylphosphine borine by pyrolysis at 200°C. proceeded to a point where the product was insoluble in all solvents tested and showed no softening point. Lower temperatures will be used in further experiments.



TABLE V

Preparation of Glass Cloth Reinforced Laminates  
from Methyl- $\beta$ -hydroxyethylphosphine Borine Adduct

Experiment No.	Resin Content, %		Differential Resin Loss %	Curing Cycle		
	Before Pressing	After Pressing		Time, hrs.	Temp, °C.	Ram Force Tons
1151-94 (Adduct)	36.0	13.2	22.8	1.5	260	0
1151-97 (Prepolymer)	37.7	24.6	13.1	2	260	5



## B. Experimental

### 1. P-Methylsesquimethyleneborophane Polymer

The experimental procedures used were essentially the same for each of the laminates prepared and, accordingly, only a general procedure is described.

#### a. Prepolymerization of 1,3-Trimethylene-P,P'-bis(methylphosphine borine) (1391-66)

A 1.8581 g. (11.3439 mmoles) quantity of 1,3-trimethylene-P,P'-bis(methylphosphine borine) was placed in a 25 ml. glass bomb tube and the evacuated sealed tube was placed in a constant temperature bath at 202°C. After a given time the tube was removed, cooled, and the hydrogen was measured in the high vacuum line. The tube was resealed and the process was repeated. The product was observed to be fluid at 202°C. after 3 hrs. but was solid after 3.33 hrs.

#### b. Purification of Oxidized 1,3-Trimethylene-P,P'-bis(methylphosphine Borine) (1151-78)

A 42.0 g. quantity of impure 1,3-trimethylene-P,P'-bis(methylphosphine borine) was dissolved in 50.0 ml. of benzene in an argon-filled separatory funnel and twice washed with 21 ml. portions of distilled water. The solution was dried over anhydrous sodium sulphate. The major portion of the benzene was removed at ambient temperature at 15 mm. pressure during 4 hrs. after which the remaining solvent was removed at 50°C. and 10 mm. during 2 hrs. leaving 30.8 g. (73.4% yield) of pure 1,3-trimethylene-P,P'-bis(methylphosphine borine). The infrared spectrum and index of refraction of the washed sample were identical to the data recorded immediately after preparation of 1,3-trimethylene-P,P'-bis(methylphosphine borine).

#### c. Percentage Resin in the Laminate

Six pieces of Type 181 glass cloth were cut using a 1.5-in. diameter arch punch and weighed to 0.01 g. on a torsion balance. The cloth circles were then individually coated with polymer solution (50% by weight in toluene) and air dried for 15 min. at room temperature, followed by 10 min. at 100°C. After removal of the solvent the polymer coated discs, which were non-tacky and readily handled, were then weighed to determine the resin content by difference. After the laminate was formed, it was reweighed to determine by difference the loss in weight of resin during the pressing operation (see Table III). In laminates that were prepared using the solid polymer, the procedure was the same except that the powdered polymer was placed between each layer of glass cloth and weighed before laminating.

#### d. Laminating Procedure

The laminates were pressed between 8 in. x 8 in. chrome-plated steel plates using 1/16 in. metal spacers. To facilitate removal of the laminate after curing the chrome plates were coated before use with a parting agent consisting of 7 parts by weight high vacuum silicone grease, 3 parts by



weight paraffin wax dissolved to 20% solids in a mixture of equal parts toluene, acetone, and carbon tetrachloride.

The stack of coated cloth circles between the chrome plates was placed in the preheated press. The press was closed and after 3 minutes pressure on the ram was raised to 5 tons. During the 1-2 hr. curing cycle the pressure increased in most experiments to a final value of 6 tons. The laminates were either removed hot at the end of the curing cycle or after cooling the press by circulating cold water through the platens.

e. Heat Distortion Temperature

Two standard epoxy formulations were prepared for use in heat distortion comparison tests. Samples 70-1 and 70-2 were prepared from a formula consisting of 100 parts by weight of Epon 828 (Shell Chemical Co. bisphenol-epichlorohydrin resin) and 14 parts by weight of m-phenylenediamine. The amine was dissolved in the resin and after thorough mixing, the resulting solution was deaerated under reduced pressure. A portion was cast into a 1/8 in. panel and the remaining resin solution was used to form a 1/8 in., 12-ply glass cloth laminate. Both the casting and the laminate were subjected to the same curing cycle of 4 hrs. at 120°C. followed by 6 hrs. at 175°C. After curing, two 5 x 1/2 in. test specimens were cut from the cast panel and two from the laminate. Sample 71 was prepared from a formula consisting of 100 parts by weight of Epon 828 and 10 parts by weight of diethylenetriamine cured at room temperature for 15 hrs., followed by 4 hrs. at 115°C. The same number of test specimens were prepared following the procedure described above.

The P-methylsesquimethyleneborophane polymer laminate (Sample 86) was formed using the procedure described previously and cured at 260°C. for 2 hrs. in the press. All samples were allowed to remain at ambient temperature for 48 hrs. before testing.

The heat distortion apparatus was constructed following the published description,<sup>2</sup> using Dow Corning 710 fluid as the heating medium. The heat distortion temperatures of the cast samples were determined under a 264 psi load. For the corresponding laminates, a load of 1377 psi was found necessary to reproduce the heat distortion temperature. This same increased load was then applied to the poly-P-methylsesquimethylene borophane laminate. The results are listed in Table IV.

f. Thermal Stability of Poly-P-methylsesquimethyleneborophane (1151-74)

A 0.1503 g. quantity of poly-P-methylsesquimethyleneborophane (polymerized at 202°C. for 12 hrs.) was placed in a sealed evacuated glass tube and heated in a tube furnace at 320°C. for 1 hr. The solid polymer had changed to a tacky semi-solid mass. The tube was opened on the vacuum line and 13.47 cc. of hydrogen and 0.14 cc. of methane were obtained. The residue weighed 0.1464 g.



## 2. Resin from Methyl- $\beta$ -hydroxyethylphosphine and Diborane

### a. Synthesis of Borine Adduct of Methyl- $\beta$ -hydroxyethylphosphine (1151-92)

Into a 1000 ml. bulb containing 30 ml. of benzene was condensed 6.52 g. (70.9 mmoles) of methyl- $\beta$ -hydroxyethylphosphine. To the resulting solution 792 cc. (35.4 mmoles) of diborane was added and the bulb was sealed and allowed to stand at room temperature for 15 hrs. The bulb was opened on the vacuum line and 1127.1 cc. (71.9% based on Equation 3) of hydrogen was collected. The product was a clear liquid, the infrared spectrum of which showed bands at 3540 (O-H) and 1338  $\text{cm}^{-1}$  (B-O-C, tricoordinate) in addition to C-H, B-H and P-H absorptions.

### b. Preparation of Prepolymer (1151-95)

A prepolymer was formed by heating 6.3 g. of the borine adduct of methyl- $\beta$ -hydroxyethylphosphine at 180°C. for 2 hrs. after a 15 hr. heating period at 110-120°C. caused no apparent increase in the viscosity. The hydrogen evolved was found to be an additional 887.0 cc. corresponding to a total of 64.9% of the theoretical based on two moles of hydrogen per mole of phosphine. The prepolymer was a white solid having a softening point of 90-100°C. (Fisher-Johns melting point apparatus) and soluble in ethanol but insoluble in benzene, toluene or xylene.

### c. Preparation of Laminates (1151-94,97)

Six 1.5 in. diameter pieces of Type 181 glass cloth were saturated with the adduct and heated under an argon atmosphere at 260°C. for 1.5 hrs. in the hydraulic press. Platens were in the closed position; however, no measurable pressure was applied. During the first 5 min. vapor escaping from between the closed platens ignited on reaching the atmosphere. In another experiment six 1.5 in. diameter pieces of Type 181 glass cloth were saturated with a 50% solution of prepolymer. The solvent was removed under vacuum at room temperature and the resin impregnated glass cloth was stacked in the press at 260°C. and 5-ton pressure applied for 2 hrs. under an argon atmosphere.

## 3. Methylborophane Polymer (1151-98,102)

Methylphosphine borine was prepared from 0.915 g. (19.0 mmoles) of methylphosphine and 212.8 cc. (9.68 mmoles) of diborane in an evacuated 1000 ml. bulb at -78°C. The bulb was sealed and heated to 204°C. for 9 hrs. to give a yellow solid and 595.6 cc. (26.6 mmoles, 70.0% yield) of hydrogen. The prepolymer was insoluble in benzene, toluene, xylene, acetone, methylethyl ketone, methylisobutyl ketone and dimethylformamide and showed no softening point up to 300°C. indicating it was too highly cross-linked to be of value.

In a second experiment, 2.20 g. (45.9 mmoles) of methylphosphine and 513.6 cc. (22.9 mmoles) of diborane were used to prepare methylphosphine



borine in the manner described above. The adduct was heated in a sealed evacuated bulb at 180°C. for 20 min. and yielded a yellow foamed solid and 996.7 cc. (44.4 mmoles, 48.4% yield) of hydrogen. A small quantity of hydrogen was lost inadvertently but is estimated not to raise the yield above 51%. The prepolymer was again insoluble in the same solvents and did not soften on heating to 300°C.



### III. BORON-PHOSPHORUS POLYMER CHEMISTRY

#### A. Discussion

##### 1. Linear Borophane Polymers

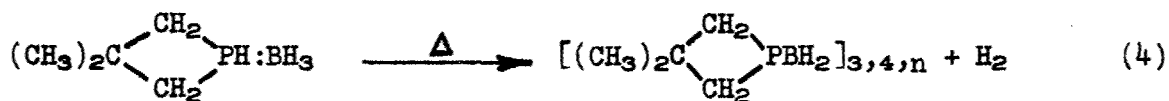
##### a. Preparation of Linear and Cyclic Methyl-n-alkyl- and Methylphenylborophane Polymers

A series of methyl-n-alkylphosphine borines ( $C_3-C_8$ ) and methylphenylphosphine borine were pyrolyzed in the presence of ca. 20 mole per cent triethylamine to: (1) extend the scope of phosphorus substituents on the resulting linear borophane polymers<sup>5,6</sup>, and (2) to determine the effect of these substituents on the degree of polymerization and yield of the linear polymers. Each of these experiments was performed on an approximate 0.13 mole scale in a stainless steel pressure vessel, and the cyclic triborophane by-product was removed by distillation on a rotary molecular still. With increased chain length of the alkyl group the residual linear borophane polymers showed: (1) a decreasing trend in the degree of polymerization (from 34 to 4.8, although  $C_7$  preceded  $C_8$ ), and (2) an apparent increase in polymer yields. The chain length of P-methylphenylborophane polymer was of the same order of magnitude (D.P. 6.2) as the  $C_6-C_8$  alkyl derivatives but the yield (24%) was only half as great. Each of the linear polymers was a glass or very viscous liquid.

The by-product triborophanes were each washed with methanolic hydrochloric acid to remove residual triethylamine and redistilled to give colorless liquids with the exception of 1,3,5-trimethyl-1,3,5-triphenyltriborophane which slowly crystallized to a waxy solid on standing. The observation that viscosity appeared to increase with increasing chain length of the n-alkyl group in 1,3,5-trimethyl-1,3,5-tri-n-alkyltriborophanes was confirmed by measurements on the n-butyl- and n-octyl-derivatives.

##### b. Preparation of P-(3,3-Dimethylcyclo-trimethylene)borophane Polymers

3,3-Dimethylcyclo-trimethylenephosphine was treated with excess diborane to form the corresponding phosphine borine, which was converted without isolation to a mixture of borophane polymers in 94.9% yield to determine the effect of the CPC bond angle on the ratio of linear to cyclic polymer formation.



Sublimation of the mixture and subsequent vapor phase chromatographic analysis of the sublimate indicated the composition to be 83.2% P-tris(3,3-dimethylcyclo-trimethylene)triborophane, 2.0% P-tetrakis(3,3-dimethylcyclo-trimethylene)-



tetraborophane, and 14.8% P-(3,3-dimethylcyclotrimethylene)borophane polymer (D.P. = 5.9). Only the triborophane, m.p. 165°C., has been characterized.

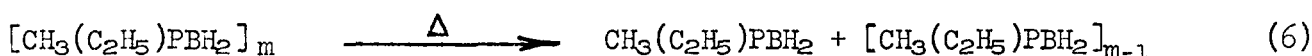
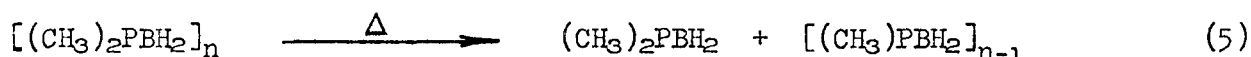
c. Thermal Decomposition of Linear Borophane Polymers

(1) P-Dimethylborophane Polymer

To elucidate further the mode of thermal decomposition of P-dimethylborophane polymer, a sample was subjected to thermal decomposition for 21 hrs. at 180°C. Hydrogen was evolved during the first stages of the decomposition together with minor amounts of condensable gases. The molecular weight of the residual polymer showed a moderate increase. These results confirm the report of Burg<sup>7</sup> who postulated some chain termination with BH<sub>3</sub> groups.

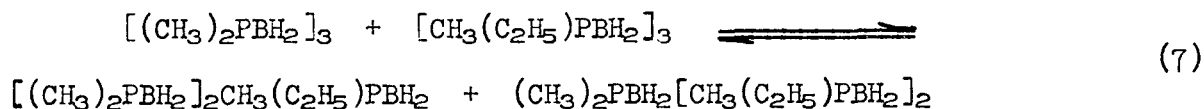
(2) P-Dimethylborophane and P-Methylethylborophane Polymer Mixtures

In two separate experiments mixtures of P-dimethylborophane and P-methylethylborophane polymers were heated for 24 hrs. at 190°C., one in the presence of a small amount of hydrogen chloride to determine the possible effect of block polymerization on the properties of the resulting polymer. The isolated polymer from the hydrogen chloride-treated mixture showed a molecular weight of 1400, indicating considerable degradation. In both cases the decomposition products were mixtures of nearly identical composition consisting of all four of the possible triborophanes comprised of one or both of the two borophane monomers. These data suggest that the polymers decomposed into monomer units according to the equations



and recombined at random to the triborophane compounds  $[(CH_3)_2PBH_2]_3$ ,  $[(CH_3)_2PBH_2]_2CH_3(C_2H_5)PBH_2$ ,  $(CH_3)_2PBH_2[CH_3(C_2H_5)PBH_2]_2$ , and  $[CH_3(C_2H_5)PBH_2]_3$ .

To confirm the postulated depolymerization of the linear polymer to monomeric units followed by random trimerization to give the observed products, an experiment was run to show that an equimolar mixture of P-hexamethyltriborophane and 1,3,5-trimethyl-1,3,5-triethyltriborophane would not undergo random reorganization (Equation 7) under the same experimental conditions. If such a reorganization occurred to any degree at moderate temperatures, the thermal stability of the P-B bond would be poor. No

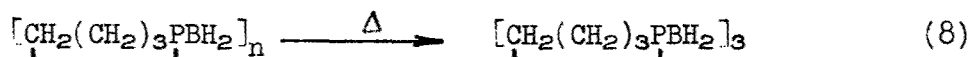




reorganization was observed to occur during 24 hrs. at 180°C. and only a few per cent reorganization was observed at 320°C. in the same time.

(3) P-Cyclotetramethyleneborophane Polymer

The linear P-cyclotetramethyleneborophane polymer (formerly believed to be P-tetrakis(cyclotetramethylene)tetraborophane<sup>8</sup>), which had been prepared in the absence of excess base, was subjected to mild pyrolysis.



Depolymerization gave as the principal product P-tris(cyclotetramethylene)tri-borophane which is compelling evidence for a linear configuration of the same monomer units in the polymer.

(4) P-(3,3-Dimethylcyclotri-methylene)borophane Polymer

The presumably linear P-(3,3-dimethylcyclotrimethylene)-borophane (D.P. 5.9), prepared in the absence of excess base (vide supra), was subjected to mild pyrolysis. Thermal depolymerization gave some P-tris-(3,3-dimethylcyclotrimethylene)triborophane but the major product showed marked spectral differences in the infrared. The data do not distinguish between a linear polymer and one resulting from opening of the tetratomic phosphine ring.

d. Reactions of Linear Borophane  
Polymers with Hydrogen Chloride

(1) P-Dimethylborophane Polymer

In two large-scale experiments attempts were made to increase the molecular weight of P-dimethylborophane polymer by treatment with hydrogen chloride. Although previous experiments<sup>4</sup> had shown large increases in molecular weight, these results seemingly could not be duplicated, presumably because of the erratic behavior of the Neumayer apparatus observed during determination of the molecular weights.

(2) P-Methylethylborophane Polymer

P-Methylethylborophane polymer reacted with hydrogen chloride with an increase in the molecular weight from 2260 to 3530. A film cast from this material seemed no different than that cast from starting material in that both films were brittle.



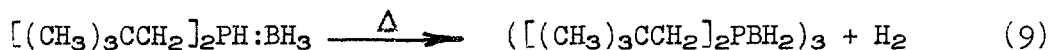
## 2. Cyclic Borophane Polymers

### a. Characterization of 1,3,5-Tri-methyl-1,3,5-triphenyltriborophane

1,3,5-Trimethyl-1,3,5-triphenyltriborophane, obtained as a viscous liquid distillate after molecular distillation,<sup>9</sup> crystallized on standing. Since this material should be a mixture of stereoisomers an attempt was made to isolate the individual components. After a cursory survey of solubility in common solvents (Table VI), hexane was selected as the recrystallizing solvent. Slow crystallization from this solvent gave two distinctly different crystal forms which were isolated mechanically and used as seed crystals to obtain larger quantities by fractional crystallization. The two materials, which had essentially the same molecular weight (403 and 400), showed marked differences in melting point (126°C. and 81°C.). Infrared and elemental analyses suggest that these compounds are the two stereoisomers. Separate solubility curves (Fig. 2) for the two stereoisomers in hexane were determined from the data in Table VII. A very small amount of a third crystal form was observed to have a melting point (126°C.) and molecular weight (406) virtually identical with one of the major components but was characterized as methylphenylphosphinic acid by comparison with an authentic sample.

### b. Preparation of P-Hexaneopentyltriborophane

Pyrolysis of crude dineopentylphosphine borine at 200°C. gave a good yield of impure P-hexaneopentyltriborophane from which pure material was isolated by fraction sublimation and crystallization in 30% yield. Whether the source of a yellow glassy material obtained as a coproduct was from impurities in the original adduct or the adduct itself was not determined.



### c. Preparation of 1,3,5-Trineo-pentyl-1,3,5-triphenyltriborophane

A mixture of the stereoisomers of 1,3,5-trineopentyl-1,3,5-triphenyltriborophane was prepared by pyrolysis of neopentylphenylphosphine borine and separated by fractional crystallization. An attempt to prepare the same material from sym-dineopentylidiphenylbiphosphine bis(borine) was unsuccessful.

### d. Preparation of 1,3,5-Trimethyl-1,3,5-tris(3-dimethylaminopropyl)triborophane

As part of a continuing effort to modify cyclic triborophane compounds to use as monomers for laminating resins, the synthesis of an epoxy-substituted triborophane was undertaken. Since the epoxy function is incompatible with the RPH<sup>-</sup> and BH<sub>3</sub> functions required as intermediates in the usual syntheses of triborophanes, a compatible functional group which could be converted to an epoxy group after synthesis of the triborophane was required.



TABLE VI

Approximate Solubilities of 1,3,5-Trimethyl-1,3,5-triphenyltriborophane

Solvent	Triborophane wt., g.	Solvent wt., g.	Volume of Solvent for Complete Solution, ml.	Approx. Minimum Solubility g./100 g. Solvent
Benzene	0.531	0.268	0.3	198
Acetone	0.699	0.397	0.5	176
Toluene	0.661	0.441	0.5	150
Chloroform	0.593	0.441	0.3	134
Ether	0.546	0.469	0.7	116
Carbon Tetrachloride	0.690	0.785	0.5	88
Hexane	0.244	2.43	3.7	10
Methanol	*	-	10	v. sl. sol.
Water	*	-	ins.	ins.

\*

Small unweighed crystal



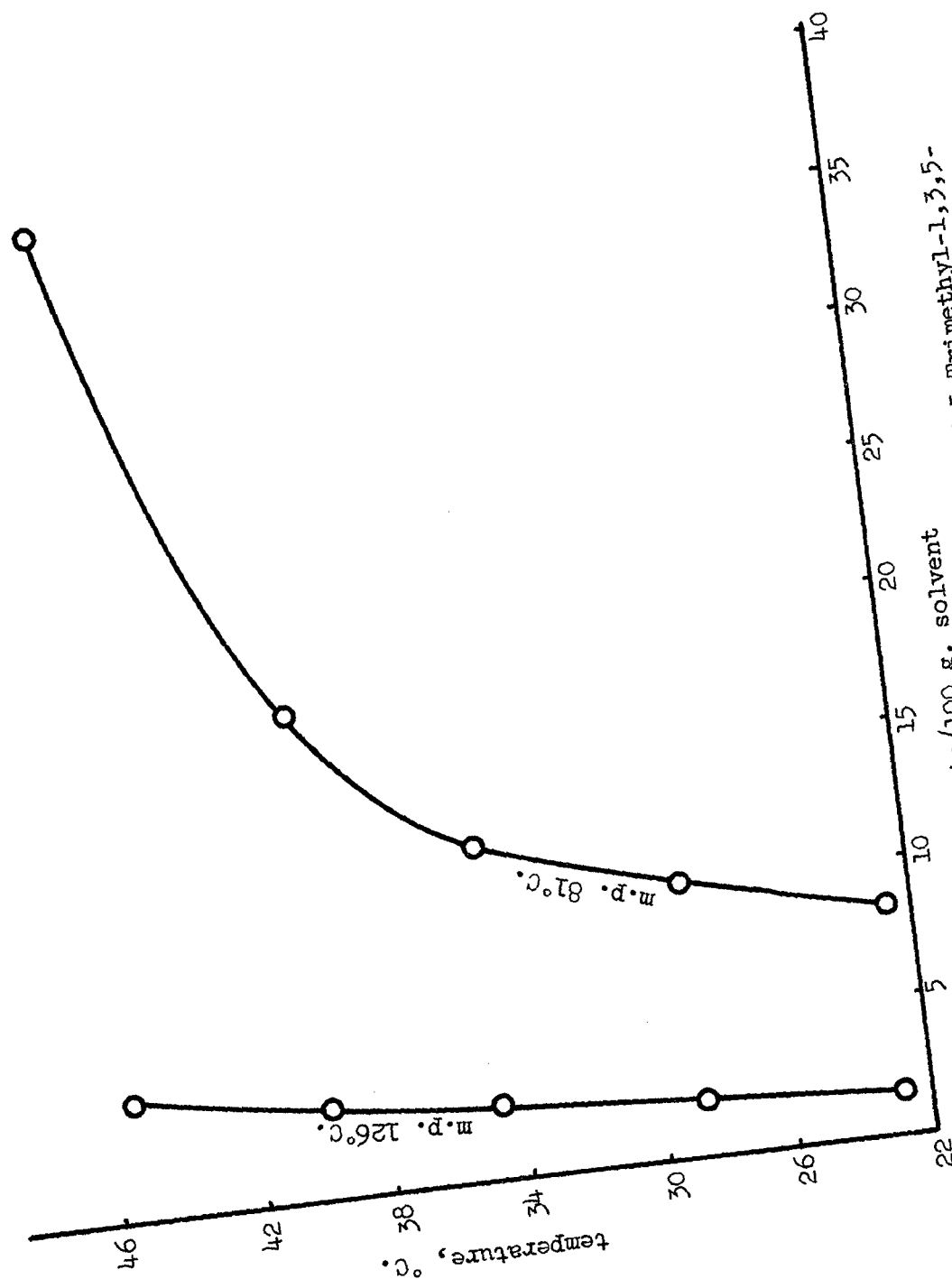


FIGURE 2. Solubility of the Stereoisomers of 1,3,5 Trimethyl-1,3,5-Triphenyltriborophane in n-Hexane.



TABLE VII

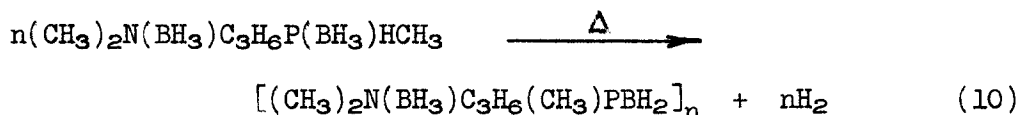
Solubility of the Stereoisomers of 1,3,5-Trimethyl-  
1,3,5-Triphenyltriborophane in n-Hexane

Temp., °C.	Solubility, g./100 g. Solvent	
	m.p. 81°C.	m.p. 126°C.
22.8	8.43	1.67
28.6	10.04	2.08
34.5	12.15	2.78
39.5	17.24	3.39
45.2	35.76	4.32

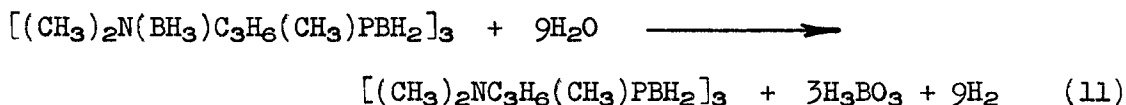


A tertiary amine function exhibits the necessary reactivity and, accordingly, was incorporated into the intermediate phosphine, methyl-3-dimethylaminopropylphosphine which, in turn, was converted to the bis(borine) adduct.

Pyrolysis of pure methyl-3-dimethylaminopropylphosphine bis(borine) produced the theoretical hydrogen based on equation (10) whereas less pure sample yielded a greater quantity of hydrogen suggesting perhaps that dissociation and subsequent degradation of the borine group associated with the nitrogen had occurred.



To attempt to isolate the triborophane derivative from the resulting liquid product which probably contains the tetraborophane derivative in addition to having tertiary amine functions both free and complexed with borine, the mixture was hydrolyzed with hydrochloric acid. On basifying the mixture the tertiary amine derivatives were obtained as a liquid mixture but the quantity was too small to attempt separation of the tri- and tetraborophanes by distillation.



- e. Attempt to Prepare a Derivative of  
1,3,5-Trimethyl-1,3,5-tris(3-dimethyl-  
aminopropyl)triborophane Suitable for  
Fractional Crystallization

To simplify the characterization of the series of triborophane derivatives leading to an epoxy-substituted triborophane, several attempts were made to prepare a derivative of 1,3,5-trimethyl-1,3,5-tris(3-dimethylaminopropyl)triborophane, which could be purified by fractional crystallization. The problem is doubly difficult, first, because there are two stereoisomers of the triborophane as well as a greater number of tetraborophane isomers which may be present and, second, because of the trifunctionality of the triborophane molecule.

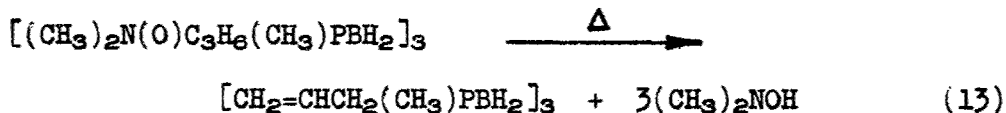
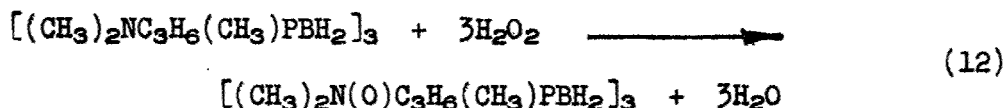
An attempt to convert the crude tertiary triamine to the tris(amine borine) was unsuccessful in that only an estimated 84% of the diborane was complexed by the base resulting in a semi-solid mass. The tris(ammonium chloride) and the tripicrate derivatives gave only oils on attempted recrystallization. The quaternary tris(ammonium iodide) turned to a sticky paste on attempted recrystallization as did the tris(ammonium tetraphenylborohydride) on attempts to coagulate the seemingly colloidal solid.



Conversion of the crude amine function to the amine oxide (vide infra) again gave a semi-solid which held methanol tenaciously.

f. Preparation of 1,3,5-Trimethyl-1,3,5-triallyltriborophane

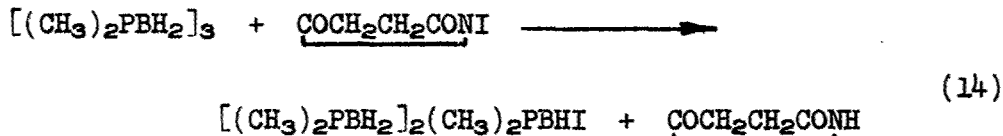
The formation of 1,3,5-trimethyl-1,3,5-tris(3-dimethylaminoxypropyl)triborophane from the crude amine appeared to proceed smoothly in methanolic hydrogen peroxide. The thermal decomposition of the amine oxide also proceeded well except that apparently before all three of the amine oxide groups on a triborophane ring have decomposed the molecule becomes more volatile, and some amine oxide groups remain in the distilled 1,3,5-trimethyl-1,3,5-triallyltriborophane. If the crude amine oxide is pyrolyzed without allowing the olefin to distill from the reaction zone excessive resin formation occurs. This phenomenon will be investigated further.



g. Preparation of B-Halo-substituted Triborophanes

(1) P-Hexamethyl-B-iodotriborophane

Two large-scale preparations of P-hexamethyl-B-iodotriborophane from P-hexamethyltriborophane and N-iodosuccinimide gave yields of 62 and 68%. In the larger preparation the sublimation residue was investigated further and found to contain a new material (possibly a polyiodotriborophane) less volatile and higher melting than the iodotriborophane.



(2) P-Hexamethyl-B,B'-diiodotriborophane

Treatment of P-hexamethyltriborophane with two moles of N-iodosuccinimide gave a complex mixture consisting of starting material and partially iodinated triborophanes. Fractional crystallization eventually provided a small quantity of a pure P-hexamethyl-B,B'-diiodotriborophane which was characterized by elemental analysis and molecular weight although the



stereoisomerism of the halogens has not been resolved.

(3) Attempt to Prepare P-Hexa-  
methyl-B-hexaiodotriborophane

Employing the procedure recently reported for the preparation of P-hexaethyl-B-hexaiodotriborophane, P-hexamethyltriborophane was treated with excess iodine in boiling ethyl iodide. As determined by molecular weight measurement a mixture of only partially iodinated materials was formed.

(4) P-Hexamethyl-B,B'-dibromotriborophane

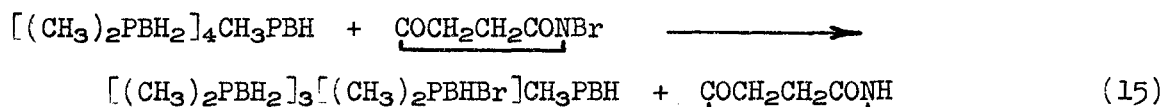
A large-scale preparation of P-hexamethyl-B,B'-dibromotriborophane from P-hexamethyltriborophane and N-bromosuccinimide utilizing nearly the same procedure as previously described<sup>11</sup> provided the product in high yield contaminated with small amounts of by-product P-hexamethyl-B-bromotriborophane and P-hexamethyl-B,B',B''-tribromotriborophane. The mixture was separated into its components by preparative vapor phase chromatography and the dibromo fraction was separated further by fractional crystallization into two isomeric compounds.

(5) P-Hexamethyl-B,B,B',B''-  
tetrabromotriborophane

P-Hexamethyltriborophane reacts with four equivalents of N-bromosuccinimide to give in low isolated yield a tetrabromo-derivative indicated by infrared analysis to be a stereoisomer of P-hexamethyl-B,B,B',B''-tetrabromotriborophane.

(6) P-Nonamethyl-B-bromobicyclo[4.4.0]-  
pentaborophane Isomers

N-Bromosuccinimide reacted with P-nonamethylbicyclo[4.4.0]pentaborophane at room temperature to give a mixture from which two monobrominated derivatives were isolated by fractional crystallization



Recrystallization of the more abundant (35.4% yield) and higher melting (m.p. 143-144°C.) isomer from methanol provided a material sufficiently pure for structure elucidation by X-ray crystallography. The infrared spectrum of the higher melting bromo-substituted isomer was virtually identical with that of the lower melting B-iodo-substituted isomer of P-nonemethylbicyclo[4.4.0]pentaborophane<sup>12</sup> strongly suggesting that the halogens are on the same boron atom and in the same stereochemical configuration. The infrared spectrum of the less abundant (16.1% yield) and lower melting (m.p. 123.5-125.0°C.) isomer was closely similar to that for the higher melting P-nonamethyl-B-iodobicyclo[4.4.0]pentaborophane isomer; again suggesting that the halogens



occupy the same stereochemical position in the molecule.

(7) P-Hexamethyl-Poly-B-Chloro-triborophanes

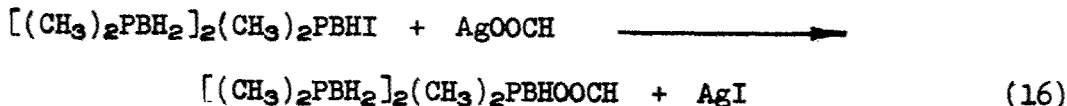
P-Hexamethyltriborophane and N-chlorosuccinimide in a 1:3 molar ratio reacted during 6 hrs. in carbon tetrachloride to give a mixture of 8.86% dichloro-, 45.3% trichloro-, 39.3% tetrachloro-, 3.3% penta-chloro-, and 0.44% hexachloro-derivatives which on attempted separation by preparative vapor phase chromatography were contaminated with gross quantities (10-15%) of unknown materials retained in the instrument.

h. Preparation of Other B-Substituted P-Hexamethyltriborophanes from B-Halo-Derivatives

(1) Carboxylate Derivatives

(a) P-Hexamethyl-B-formoxytriborophane

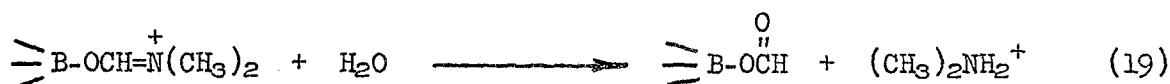
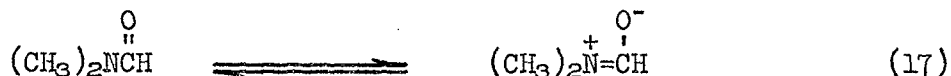
Treatment of P-hexamethyl-B-iodotriborophane with silver formate in refluxing benzene provided a crude mixture containing a carbonyl compound found to be P-hexamethyl-B-formoxytriborophane.



Vapor phase chromatographic analysis of the mixture indicated that it contained nearly 80% starting material. Fractional crystallization produced impure P-hexamethyl-B-formoxytriborophane which was identified by comparison of its infrared spectrum with that of a more fully characterized sample prepared using dimethylformamide (vide infra). The poor quality silver formate was believed to be responsible for the mixture because the reaction was incomplete.

To prove conclusively that both the product obtained from P-hexamethyl-B-iodotriborophane and silver formate and the by-product obtained from many reactions performed in dimethylformamide<sup>13</sup> solution was P-hexamethyl-B-formoxytriborophane, P-hexamethyl-B-iodotriborophane was heated at 100°C. for 5 hrs. with 90% aqueous dimethylformamide. P-Hexamethyl-B-formoxytriborophane was obtained in 67.2% yield and fully characterized by infrared and elemental analyses and molecular weight. A proposed mechanism for this reaction is as follows:



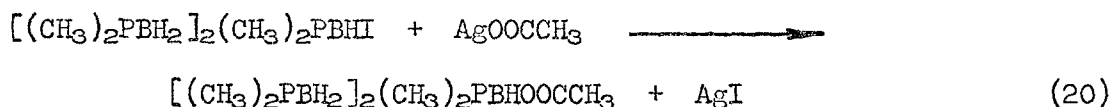


To lend support to this proposed mechanism for the interaction of halotriborophanes, amides, and water and to broaden the scope of this new reaction, P-hexamethyl-B-iodotriborophane was treated at 100°C. for 19 hrs. with aqueous formamide. P-Hexamethyl-B-formoxytriborophane was obtained in approximately 63% yield along with unreacted starting material. After recovery of the formoxy-derivative, ammonium ion was identified in the filtrate by liberation of ammonia on basification and a positive Nessler's Reagent Test.<sup>14</sup> Iodide ion was identified by precipitation as the yellow-colored silver iodide.

P-Hexamethyl-B-iodotriborophane reacted completely with aqueous formic acid to give degradation products rather than the formoxy-derivative. Infrared analysis of the ill-defined degradation products showed boric acid as the only identifiable material.

(b) P-Hexamethyl-B-acetoxytriborophane

P-Hexamethyl-B-iodotriborophane was treated with silver acetate in a refluxing benzene solution to provide a 73% yield of P-hexamethyl-B-acetoxytriborophane. The structure of the product was confirmed by its infrared spectrum with characteristic absorption bands at 1700 cm<sup>-1</sup> (C=O), 1368 cm<sup>-1</sup> (CH<sub>3</sub>-C) and 1050 cm<sup>-1</sup> (B-O-C).



Sodium acetate, in refluxing ethanol, failed to react with P-hexamethyl-B-bromotriborophane in an attempt to replace the bromine with an acetoxy group. P-Hexamethyl-B-bromotriborophane was recovered in 91% yield.

The failure of sodium acetate to react to form the B-acetoxy compound and the success with silver acetate suggests a mechanism which based on the insolubility of the silver iodide would require silver ion



to first complex with the halide, thus weakening the B-X bond allowing for displacement by acetate ion. An alternative mechanism might be envisioned whereby iodide ion is first removed by silver ion leaving a triborophane cation which would then react with acetate ion.

P-Hexamethyl-B-iodotriborophane reacted with aqueous dimethylacetamide, in a manner similar to its reaction in aqueous dimethylformamide, to provide P-hexamethyl-B-acetoxytriborophane in low yields (24.2 and 22.4%). The reason for the low yields was not apparent since reaction conditions and the work-up procedure were essentially the same as in the preparation of the formoxy-derivative. In one experiment, conducted in a sealed tube under vacuum, the moderate quantity hydrogen obtained as by-product, suggests that decomposition of the triborophane nucleus may have occurred. Comparison of infrared spectra, melting points and mixture melting points confirmed the structure of the product as the same acetoxy-triborophane derived from P-hexamethyl-B-iodotriborophane and silver acetate.

(c) B-Hexamethyl-B-benzoytriborophane

P-Hexamethyl-B-iodotriborophane reacted with silver benzoate (in the same manner indicated in equations 16 and 20) in refluxing benzene to provide an 86% yield of P-hexamethyl-B-benzoytriborophane. The trace of benzoic acid found on purification of the product was believed to have been present in the silver benzoate. Definitive characterization of the benzoy-derivative was made by elemental analysis, molecular weight and interpretation of its infrared spectrum which displayed normal benzoate absorption bands at  $1690\text{ cm}^{-1}$  (C=O),  $1297$  and  $1127\text{ cm}^{-1}$  ( $\text{C}_6\text{H}_5\text{COO}$ ) and  $1050\text{ cm}^{-1}$  (B-O-C).

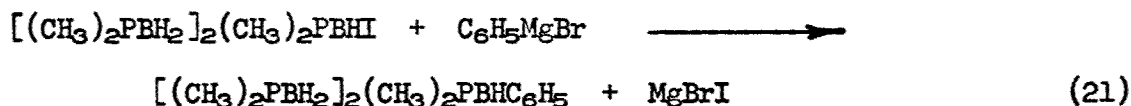
(d) Attempt to Prepare Bis(P-hexamethyl-B-iodotriborophyl) Adipate

In an unsuccessful attempt to link two triborophane rings through a di-ester, P-hexamethyl-B-iodotriborophane was heated at  $100^\circ\text{C}$ . for 8 hrs. and at  $150^\circ\text{C}$ . for 15 hrs. with aqueous adipamide. Two unknown materials, the nature of which was not established, were obtained and neither displayed carbonyl absorption bands in their infrared spectra.

(2) B-Aryl- and B-Alkyl-Derivatives

(a) P-Hexamethyl-B-phenyltriborophane and P-Hexamethyl-B,B'-diphenyltriborophane

P-Hexamethyl-B-iodotriborophane was heated with an ethereal solution of phenylmagnesium bromide at  $125^\circ\text{C}$ . in a sealed tube for 15 hrs. Sublimation of the crude reaction product yielded biphenyl and P-hexamethyl-B-phenyltriborophane (2.2% yield).





After hydrolysis of the sublimation residue, further sublimation yielded materials containing monophenyl- and diphenyltriborophanes from which only P-hexamethyl-B,B'-diphenyltriborophane (8.7% yield) could be recovered in a pure state. These results are in contrast to those previously reported<sup>15</sup> wherein less vigorous conditions were used and 96% recovery of starting material was obtained.

(b) P-Hexamethyl-B-ethyltriborophane

P-Hexamethyl-B-iodotriborophane and diethylzinc on heating at 100°C. for 10 hrs. gave a complex mixture consisting of 46.8% P-hexamethyltriborophane, 39.3% P-hexamethyl-B-ethyltriborophane, 1.3% P-hexamethyl-B,B'-diethyltriborophane and 0.2% P-hexamethyl-B,B',B''-triethyltriborophane. The monoethyl-derivative was separated and purified by preparative vapor phase chromatography and characterized by elemental analysis, molecular weight, and infrared spectrum.

(c) P-Hexamethyl-B-Poly-Methyltriborophanes

A mixture of partially B-chlorinated P-hexamethyltriborophanes was heated at 110°C. with dimethylzinc for 9 hrs. Sublimation of the residue after removal of excess dimethylzinc separated the material into three fractions. Preparative vapor phase chromatographic separation of these sublimates provided samples of each of the B-methyl substituted P-hexamethyltriborophanes suitable for purification by fractional crystallization.

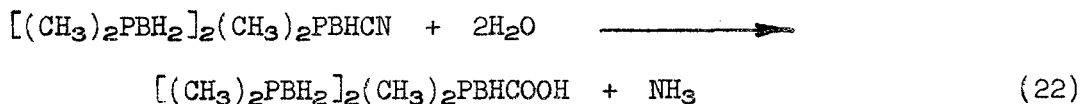
(3) Miscellaneous B-Substituted Derivatives

(a) P-Hexamethyl-B-cyanotriborophane

A larger scale preparation of P-hexamethyl-B-cyanotriborophane by the method employed previously<sup>13</sup> yielded a product which analyzed 97.9% P-hexamethyl-B-cyanotriborophane, 0.2% P-hexamethyltriborophane, 1.6% P-hexamethyl-B-iodotriborophane and 0.3% P-hexamethyl-B,B'-diiodotriborophane.

[1] Attempt to Hydrolyze  
P-Hexamethyl-B-cyanotriborophane

In an attempt to hydrolyze the cyano function to form a carboxy group, P-hexamethyl-B-cyanotriborophane was heated in aqueous sodium hydroxide for 18 hrs. at 110°C. and 24 hrs. at 150°C. in a sealed tube.

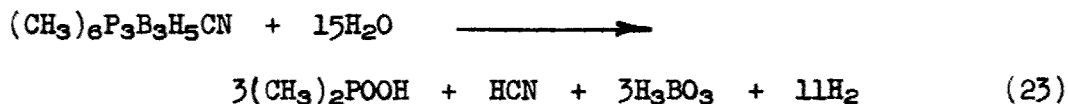


On work-up there were obtained hydrogen, a trace of methane, silicon dioxide (arising from reaction with the glass tube) and a 70% recovery of starting



material. In a second experiment, addition of ethanol to the basic medium to increase the solubility of the triborophane did not promote hydrolysis as a 91% recovery of starting material was obtained after similar heat treatment.

Treatment of P-hexamethyl-B-cyanotriborophane with concentrated hydrochloric acid heated to reflux failed to effect hydrolysis of the cyano group although only 46% of the starting material was recovered. That the triborophane nucleus was destroyed was confirmed in a second experiment wherein the cyano-derivative was heated with concentrated hydrochloric acid in a sealed tube at 155°C. for 36 hrs. to produce only water soluble products and 91% of the hydrogen indicated by equation 23.

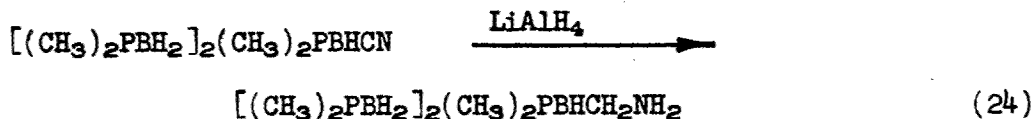


Attempted hydrolysis employing sulfuric acid in water and acetic acid under refluxing conditions also appeared to degrade the triborophane ring as neither the expected product or starting material was detectable.

P-Hexamethyl-B-cyanotriborophane failed to react with alkaline hydrogen peroxide in an attempted hydrolysis to the amide-derivative and was recovered in 92.0% yield.

[2] Attempt to Reduce P-Hexamethyl-B-cyanotriborophane

Lithium aluminum hydride in refluxing tetrahydrofuran failed to reduce P-hexamethyl-B-cyanotriborophane which was recovered in 98% yield. The small amounts of P-hexamethyl-B-iodotriborophane (1.6%) and P-hexamethyl-B,B'-diiodotriborophane (0.3%) present in the starting material were reduced to P-hexamethyltriborophane during the reaction.



Three unsuccessful attempts were made to reduce P-hexamethyl-B-cyanotriborophane with diborane. In the first two experiments, one using tetrahydrofuran as solvent and one without solvent the starting material was recovered in 98.0% and 87.6% yield, respectively, and identified by vapor phase chromatographic analysis. In a third exploratory experiment in which the borine-cyanotriborophane adduct was first prepared in pentane solution, isolated, and then pyrolyzed at 200°C. a surprisingly large quantity of P-hexamethyltriborophane was found. This material could only have formed by reductive cleavage of the cyano group. No evidence for reduction of



The cyano group to an aminomethyl group was found. Approximately 38% of the P-hexamethyl-B-cyanotriborophane was recovered.



(b) Attempt to Prepare P-Hexamethyl-B-hexacyanotriborophane

P-Hexamethyl-B-hexachlorotriborophane failed to react with silver cyanide during 11 hrs. in refluxing diglyme solution and was recovered in 80.6% yield.

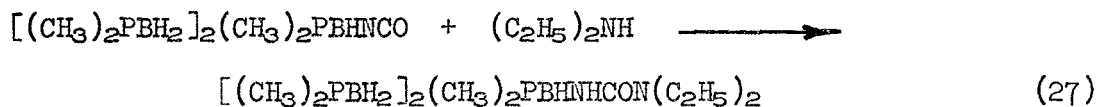
(c) P-Hexamethyl-B-isocyanatotriborophane

P-Hexamethyl-B-iodotriborophane reacted with potassium cyanate in dimethylformamide to provide an 85% crude yield of P-hexamethyl-B-isocyanatotriborophane. The product was accompanied by a small amount of side reaction product, P-hexamethyl-B-formoxytriborophane resulting from interaction of the iodotriborophane, dimethylformamide and a trace quantity of water present in the solvent (vide supra). The infrared spectrum showed a characteristic band at  $2280 \text{ cm}^{-1}$  ( $\text{N}=\text{C}=\text{O}$ ) confirming the structure assigned to this material.

Treatment of P-hexamethyl-B-iodotriborophane with silver cyanate in benzene at  $40\text{--}50^\circ\text{C}$ . provided a 55.4% yield of P-hexamethyl-B-isocyanatotriborophane admixed with starting material. A similar experiment using silver cyanate in refluxing acetonitrile failed to give P-hexamethyl-B-isocyanatotriborophane. Apparently the conditions were sufficiently severe to decompose the triborophane since no solid product was obtained.

[1] Reaction with Diethylamine.  
P-Hexamethyl-B-(3,3-diethylureido)-triborophane

P-Hexamethyl-B-isocyanatotriborophane reacted with diethylamine at  $100^\circ\text{C}$ . to provide a 94.6% crude yield of the borourea, P-hexamethyl-B-(3,3-diethylureido)triborophane.



Considerable difficulty in purification reduced the pure yield substantially. Although the observed molecular weight was high (perhaps due to association



through hydrogen bonding) the infrared absorption bands observed at 3460 (m, N-H), 1628 (vs, C=O) and 1493  $\text{cm}^{-1}$  (vs, N-H bending) substantiate the assigned structure.

## [2] Reaction with Phenol

P-Hexamethyl-B-isocyanatotriborophane failed to react with phenol at 100°C. but at 200°C. an apparent reduction reaction occurred to provide a mixture containing significant amounts of P-hexamethyl-B-cyanotriborophane as indicated by infrared and vapor phase chromatographic analyses. The data do not eliminate the possibility that an isomerization to the cyanato-derivative may have occurred. Because of the unusual nature of the reaction and the difficulty encountered in analyzing the mixture due to the similar volatilities of the components, a confirmatory experiment will be required.

### (d) Attempt to Prepare P-Hexamethyl-B,B'-diisocyanatotriborophane

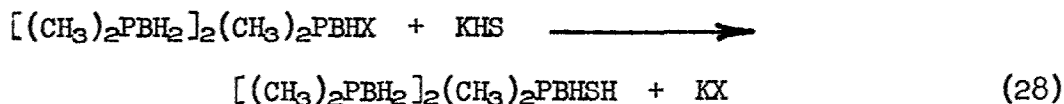
P-Hexamethyl-B,B'-dibromotriborophane failed to react with potassium cyanate in boiling absolute ethanol and was recovered in 90.5% yield.

### (e) P-Hexamethyl-B-thiocyanotriborophane or P-Hexamethyl-B-isothiocyanatotriborophane

P-Hexamethyl-B-iodotriborophane reacted readily with potassium thiocyanate at 100°C. in dimethylformamide to provide an 85% crude yield of a compound which showed a strong absorption band in the infrared at 2120  $\text{cm}^{-1}$ . Derivatives of this material must be prepared to establish whether it is P-hexamethyl-B-thiocyanotriborophane or the corresponding B-isothiocyanato compound.

### (f) P-Hexamethyl-B-mercaptotriborophane

P-Hexamethyl-B-iodotriborophane was heated under reflux in an ethanolic potassium hydrosulfide solution saturated at all times with hydrogen sulfide to provide crude P-hexamethyl-B-mercaptotriborophane contaminated with starting material. A similar reaction of P-hexamethyl-B-bromotriborophane, with sodium sulfide nonahydrate in dimethylformamide at 100°C. was found to give hydrogen, a trace of methane and P-hexamethyl-B-mercaptotriborophane characterized by its infrared spectrum, molecular weight and volatility.



When analyzed by vapor phase chromatography at 250°C. the material appeared to be nearly pure but the analytical data are subject to doubt because of the



similar retention time of the bromo-derivative used as starting material; at 300°C. the material apparently underwent extensive thermal decomposition on the chromatographic column.

(g) P-Hexamethyl-B-methanethiotriborophane

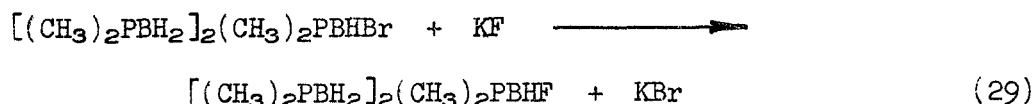
P-Hexamethyl-B-iodotriborophane reacted smoothly with sodium methanethiolate in refluxing ethanol to give a 92% yield of P-hexamethyl-B-methanethiotriborophane characterized by elemental analysis and molecular weight. Oxidation of P-hexamethyl-B-methanethiotriborophane with 30% hydrogen peroxide gave a complex mixture found to consist of five components by vapor phase chromatography. Two strong, well-defined absorption bands in the infrared at  $1093\text{ cm}^{-1}$  and  $1228\text{ cm}^{-1}$  was strong evidence that the major and least volatile component (70.0%) of the mixture was the desired sulfone. Unfortunately the bulk of the product was lost in an attempt to isolate the major component by preparative vapor phase chromatography.

(h) Reduction of P-Hexamethyl-B-bromo-triborophane with Lithium Aluminum Hydride

P-Hexamethyl-B-bromotriborophane was reduced to P-hexamethyltriborophane with lithium aluminum hydride in refluxing ether to the extent of about 13%. The reduction product was not isolated but was identified by vapor phase chromatography. P-Hexamethyl-B-bromotriborophane was the only other constituent found on chromatographic analysis of the volatile part of the reaction mixture.

(i) P-Hexamethyl-B-fluorotriborophane

Treatment of P-hexamethyl-B-chlorotriborophane with potassium fluoride in sulfur dioxide at 80°C. failed to give the monofluorotriborophane derivative, and starting material was recovered in 87.1% yield. There is question whether potassium fluorsulfite actually formed since little of the potassium fluoride had dissolved. In the reaction of P-hexamethyl-B-bromotriborophane with potassium fluoride in ethylene glycol at 100°C. during 8 hrs. a crude reaction product was obtained and shown by vapor phase chromatographic analysis to contain 8.6% of a component having volatility intermediate between P-hexamethyltriborophane and P-hexamethyl-B-chlorotriborophane.



The material is assumed to be P-hexamethyl-B-fluorotriborophane but definitive characterization must await preparation and isolation of a larger quantity of pure material.



(j) Attempt to Prepare P-Hexamethyl-B-ethoxytriborophane

Treatment of P-hexamethyl-B-iodotriborophane with an ethanolic solution of sodium ethoxide under reflux failed to give the B-ethoxy derivative. An 80% recovery of starting material was achieved.

(k) Attempt to Prepare P-Hexamethyl-B-[B-(P-hexamethyltriborophyl)]triborophane

Treatment of a refluxing ethereal solution of P-hexamethyl-B-iodotriborophane with sodium gave a complex mixture consisting of P-hexamethyltriborophane, presumably arising from a reduction reaction, starting material and small quantities of a slightly volatile crystalline solid which may be the desired P-hexamethyl-B[B-(P-hexamethyltriborophyl)]triborophane. Further work will be necessary to identify this product.

(l) Attempt to Prepare P-Hexamethyl-B-(N-pentamethylborazyl)triborophane

N-Lithiopentamethylborazene, prepared from N-dimethyl-B-trimethylborazene and ethereal methyllithium, was treated with P-hexamethyl-B-iodotriborophane in an attempt to prepare a borazyltriborophane derivative. No reaction occurred and the triborophane was recovered in 90.6% yield.

i. Reactions of P-Hexamethyltriborophane

(1) With Trimethylaluminum and Iodine

P-Hexamethyltriborophane was treated with trimethylaluminum and iodine at 125°C. for 12 hrs. Vapor phase chromatographic analysis of the crude product showed it to consist of 96.3% P-hexamethyltriborophane, 2.7% P-hexamethyl-B-methyltriborophane, and 1.0% P-hexamethyl-B,B'-dimethyltriborophane. The products are presumed to have formed by iodination of the triborophane followed by methylation with trimethylaluminum, although this experiment alone does not preclude direct attack by an intermediate  $(CH_3)_3-nAlI_n$  compound.

(2) Reaction of P-Hexamethyltriborophane with Aluminum and Organic Halides

Treatment of P-hexamethyltriborophane with aluminum metal and methyl iodide at 125°C. for an extended period of time resulted in the formation of a volatile solid product which had none of the characteristics of the expected methylated triborophanes. Instead, it appeared to be a much more reactive material, darkening in color on standing, and decomposing and/or absorbing on the chromatographic column. The infrared spectrum, decidedly not the starting material or expected products, displayed absorption bands characteristic of the P-methyl and B-hydrogen groups. No structure could be assigned to the product.



Heating of P-hexamethyltriborophane at 125°C. for 110 hrs. in the presence of aluminum metal and ethyl bromide resulted in the conversion of 13.7% of the triborophane into its B-monobromo-derivative, as determined by vapor phase chromatography.

In an attempt to arylate the triborophane nucleus in a one-step method, P-hexamethyltriborophane was heated at 125°C. with aluminum metal and iodobenzene. No product other than starting material, recovered in 77% yield, was detected.

(3) With Maleic Anhydride and Acetic Anhydride

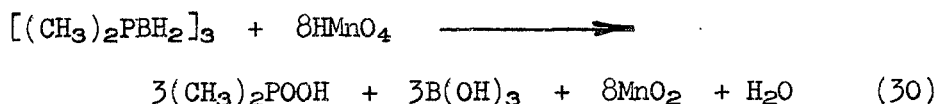
Both maleic anhydride and acetic anhydride react destructively with P-hexamethyltriborophane at 180°C. Carbon dioxide, hydrogen, and starting material were the only identifiable materials isolated from these reactions. In each case black residues of unknown constitution were formed.

(4) With Ethylene Oxide

An aluminum chloride catalyzed condensation of ethylene oxide with P-hexamethyltriborophane to yield P-hexamethyl-B-hexaethoxytriborophane failed to occur at 110°C. Instead, polyethylene oxide was formed and recovery of P-hexamethyltriborophane was nearly quantitative.

(5) With Potassium Permanganate

In an attempt to introduce a B-hydroxy function into the triborophane ring, P-hexamethyltriborophane was oxidized with potassium permanganate. Complete rather than partial oxidation occurred according to the stoichiometry of equation 30.



(6) With Picric Acid

P-Hexamethyltriborophane was added to a saturated ethanolic solution of picric acid to determine if characteristic derivatives could be prepared. The mixture was allowed to stand at room temperature for 24 hrs. without any observable change in the solution or precipitation. On work-up by cooling and/or adding water to the mixture, 55% of P-hexamethyltriborophane was recovered unchanged. However, a trace amount of unknown material with a melting point differing from the starting materials was recovered.



j. Preliminary Study of the Colored Complexes  
Derived from Triborophanes and Various  
Organometallic Compounds with Tetracyanoethylene

Preliminary studies have shown that triborophanes and tetracyanoethylene give yellow-to-brown colored solutions in methylene chloride, possibly the result of the formation of molecular complexes. Similar treatment of a number of organometallic compounds resulted in the formation of highly colored solutions believed also to indicate the formation of molecular complexes. For example, organophosphorus compounds gave red colored solutions, organo-tin derivatives gave yellow solutions and organosilanes gave yellow-to-pink colored solutions. Ultraviolet and visible spectral studies may indicate whether this reagent will give molecular complexes and establish whether there are significant spectral differences among the various triborophanes.

k. Spontaneous Ignition Temperatures of  
Some Triborophanes

Spontaneous ignition temperatures of various triborophanes were obtained using the procedure previously described<sup>16</sup>. The data obtained are shown in Table VIII.

A regularly increasing trend in spontaneous ignition temperature with increasing molecular weight was noted in the homologous series of P-trimethyl-P-trialkyltriborophanes with the exception of the methyl- and octyl-derivatives. Relative to the others these two compounds were extensively purified which is believed to account for the considerably higher ignition temperatures observed.

As anticipated on theoretical grounds the triborophanes containing boron-oxygen bonds were found to be slightly less oxidatively stable than the standard P-hexamethyltriborophane with the exception of the B-benzoyl-derivative which has much greater molecular weight and lower volatility. P-Hexamethyl-B-cyanotriborophane, however, was observed to have increased oxidative stability, supporting the premise that a B-hexacyanotriborophane would have an extremely high degree of thermal and oxidative stability.

3. Phosphine Borines

a. Preparation of 1,3-Trimethylene-  
P,P'-bis(methylphosphine borine)

An essentially quantitative yield of 1,3-trimethylene-P,P'-bis(methylphosphine borine) was prepared by treating 1,3-bis(methylphosphino)propane with diborane. This material was used as the starting material for a series of experiments in which its pyrolysis product, P-methylsesquimethyleneborophane polymer, was used as a candidate laminating resin.



TABLE VIII

Spontaneous Ignition Temperatures of Some Triborophanes

Compound	Ignition Temp., °C.
$[(CH_3)_2PBH_2]_3$	255
$[CH_3(C_2H_5)PBH_2]_3$	220
$[CH_3(C_3H_7)PBH_2]_3$	225
$[CH_3(C_4H_9)PBH_2]_3$	245
$[CH_3(C_5H_{11})PBH_2]_3$	265
$[CH_3(C_6H_{13})PBH_2]_3$	285
$[CH_3(C_7H_{15})PBH_2]_3$	295
$[CH_3(C_8H_{17})PBH_2]_3$	405
$[CH_3(C_6H_5)PBH_2]_3$ (m.p. 126°C.)	295
(m.p. 81°C.)	295
$[(C_2H_5)_2PBH_2]_3$	240
$[(neo-C_5H_{11})_2PBH_2]_3$	295
$[neo-C_5H_{11}(C_6H_5)PBH_2]_3$ (m.p. 191°C.)	325
(m.p. 104°C.)	325
$[(CH_3)_2PBH_2]_2[(CH_3)_2PBH(OOCH)]$	225
$[(CH_3)_2PBH_2]_2[(CH_3)_2PBH(OOCCH_3)]$	235-245
$[(CH_3)_2PBH_2]_2[(CH_3)_2PBH(OOCC_6H_5)]$	285
$[(CH_3)_2PBH_2]_2[(CH_3)_2PBHCN]$	275



b. Preparation of Dineopentylphosphine  
Borine and Neopentylphenylphosphine Borine

Treatment of samples of dineopentylphosphine and neopentylphenylphosphine with excess diborane resulted in quantitative conversion to the respective adducts, dineopentylphosphine borine and neopentylphenylphosphine borine.

c. Preparation of Methyl-3-dimethyl-  
aminopropylphosphine Bis(borine)

The addition of equimolar quantities of methyl-3-dimethylaminopropylphosphine and diborane proceeds rapidly and quantitatively to give the crystalline adduct, methyl-3-dimethylaminopropylphosphine bis(borine). A less clear-cut reaction, which presumably was incomplete, was observed in pentane solution.

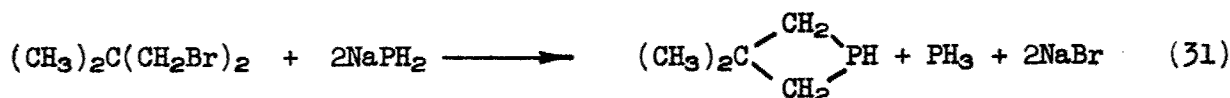
4. Organophosphines

a. Preparation of 1,3-Bis(methylphosphino)propane

A new supply of 1,3-bis(methylphosphino)propane was prepared in 75% yield and high purity as previously described<sup>17</sup> from sodium methylphosphinide and 1,3-dibromopropane for use as an intermediate in the preparation of a laminating resin.

b. Preparation of 3,3-Dimethyl-  
cyclotrimethylenephosphine

3,3-Dimethylcyclotrimethylenephosphine, the first known example of this type of tetratomic ring system, was prepared from sodium phosphinide and 1,3-dibromo-2,2-dimethylpropane, in 97% crude yield.



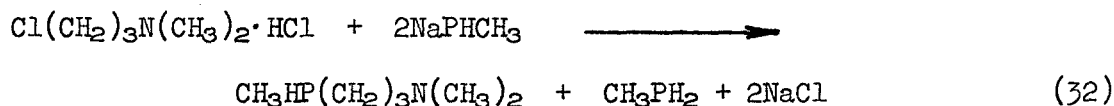
The thermal instability of this cyclic phosphine was observed in three preliminary experiments wherein the product was isolated only if maintained at low temperature (ca. -50°C.). Exposure to higher temperatures resulted in some apparent polymerization presumably by ring opening. An attempt to obtain a vapor tension curve confirmed the instability of this phosphine. The pure product was isolated in only 20% yield and characterized by infrared spectrum, vapor density molecular weight (calcd. 102.1, found 103.1), and by formation of the borine adduct.

c. Preparation of Methyl-3-dimethylaminopropylphosphine

In the continuing effort to prepare a triborophane carrying



a functionally substituted alkyl group, methyl-3-dimethylaminopropylphosphine assaying 99% pure was synthesized as an intermediate from sodium methylphosphinide and 3-dimethylaminopropyl chloride hydrochloride in 49 and 61% yields, respectively.



An attempt to introduce the two phosphorus substituents in reverse order, starting with sodium phosphinide and 3-dimethylaminopropyl chloride hydrochloride followed by methylation, gave only a 4% yield of the secondary phosphine.

d. Preparation of Methyl-β-hydroxyethylphosphine

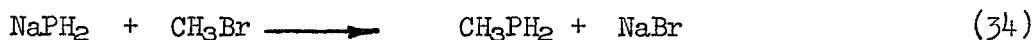
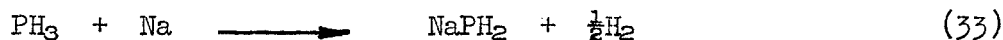
A new functionally substituted secondary phosphine, methyl-β-hydroxyethylphosphine, has been prepared in 50% yield from sodium methylphosphinide and ethylene oxide for possible use as an intermediate in the preparation of a laminating resin.

e. Attempt to Prepare Methyl-2-(benzyloxy)ethylphosphine

To prepare a triborophane carrying a hydroxy substituted alkyl group, which might be useful as a cross-linking function, a protective group must be used to prevent reaction to the protonic and hydridic functional groups. Unsuccessful attempts were made to prepare methyl-2-(benzyloxy)ethylphosphine, in which the benzyloxy function acts as the protective group, from either sodium methylphosphinide, ethylene oxide and benzyl chloride under two sets of reaction conditions or from sodium methylphosphinide and 1-chloro-2-benzyloxyethane.

f. Attempt to Improve the Organo-phosphine Synthetic Process I

In an attempt to improve Process I<sup>18</sup> for preparing organophosphines used as intermediates in the production of bench-scale quantities of boron-phosphorus compounds, it was found that liquid ammonia is required only to produce the intermediate sodium phosphinide (Equation 33). Upon replacement of liquid ammonia by toluene at this stage, alkylation to form methylphosphine was accomplished in an estimated 85% yield.





An attempt to substitute toluene for liquid ammonia in the first step was unsuccessful because the required sodium phosphinide intermediate failed to form readily in toluene.

g. Preparation of Tris-(dimethylamino)phosphine

Tris(dimethylamino)phosphine was prepared from phosphorus trichloride and dimethylamine in 71.3% yield and used for calibration of the gas chromatograph.

h. Preparation of Dimethylaminoneopentylphenylphosphine and Dimethylaminodineopentylphosphine

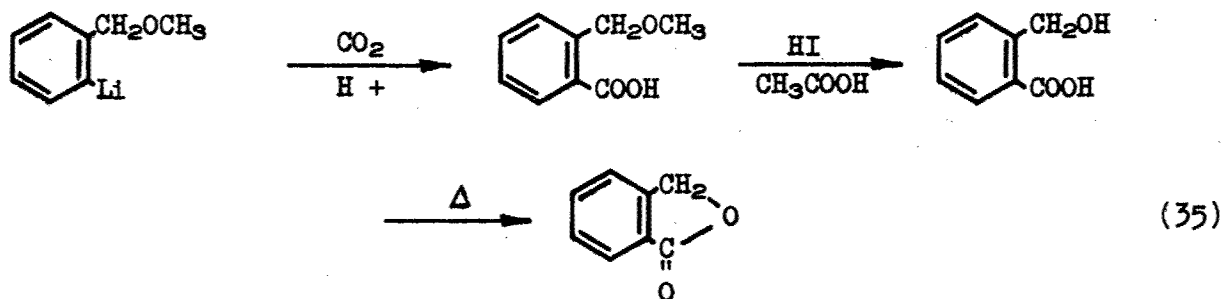
For the purpose of preparing triborophane derivatives with improved oxidative stability relative to P-hexamethyltriborophane, preparation of a series of intermediates leading to neopentylphenyl- and dineopentylphosphines was initiated. Presumably the greater steric requirements of these two substituents should provide oxidizing agents less ready access to the triborophane ring. Accordingly, dimethylaminophenylchlorophosphine was prepared by partial dimethylaminolysis of phenyldichlorophosphine and converted to dimethylaminoneopentylphenylphosphine by reaction with neopentylmagnesium chloride. In the same manner, dimethylaminodineopentylphosphine was synthesized by reaction of dimethylaminodichlorophosphine with the neopentyl Grignard reagent.

i. Attempt to Prepare o-Bis(dimethylamino)-phosphinobenzyl Methyl Ether

(1) o-Lithiobenzyl Methyl Ether

Three preparations of o-lithiobenzyl methyl ether<sup>18</sup> from n-butyllithium and o-bromobenzyl methyl ether were made for use as an intermediate in the preparation of 2,3-benzocyclotrimethylenephosphine. The ultimate objective is to determine if a borophane with a tetratomic phosphorus-containing heterocyclic substituent will promote formation and stabilization of linear borophane polymers.

The product was characterized by conversion to the o-methoxymethyl benzoic acid and phthalide derivatives (Equation 35).





(2) o-Bis(dimethylamino)phosphino-  
benzyl Methyl Ether

An unsuccessful attempt was made to synthesize o-bis-(dimethylamino)phosphinobenzyl methyl ether from o-bromobenzyl methyl ether and bis(dimethylamino)chlorophosphine for use as an intermediate in the preparation of 2,3-benzocyclotrimethylenephosphine. When synthesized, this phosphine will be used to obtain confirmatory evidence for formation of linear borophane polymers promoted by the tetratomic phosphorus-containing heterocyclic substituent.

j. Preparation of Neopentylphenylchloro-  
phosphine and Dineopentylchlorophosphine

The dimethylamino blocking groups in dimethylaminoneopentyl-phenylphosphine and dimethylaminodineopentylphosphine were readily removed by reaction with anhydrous hydrogen chloride to give the respective chlorophosphines in 59% and 74% yields.

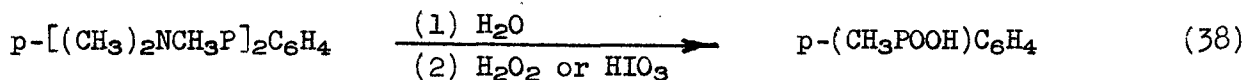
k. Preparation of Neopentylphenyl-  
phosphine and Dineopentylphosphine

Addition of neopentylphenylchlorophosphine to ethereal lithium aluminum hydride produced primarily neopentylphenylphosphine with some sym-dineopentylbiphenylbiphosphine whereas the reverse addition of reagents gave only the biphosphine derivative. Unexpectedly the reverse addition of lithium aluminum hydride to dineopentylchlorophosphine produced dineopentylphosphine rather than the biphosphine derivative.



l. Preparation of Disubstituted  
Aromatic Phosphorus Compounds

To prepare p-bis(methylphosphino)benzene<sup>20,21</sup> by an independent synthesis, the following sequence of reactions was undertaken:





p-Bis(dimethylaminomethylphosphino)benzene (Equation 37) was not obtained in a pure state but used directly to prepare benzene-1,4-bis(methylphosphinic acid) (Equation 38) which was isolated and well characterized. The formation of the acid chloride using thionyl chloride followed by in situ reduction failed to give p-bis(methylphosphino)benzene.

## 5. Miscellaneous Intermediates

### a. Preparation of Neopentyl Chloride

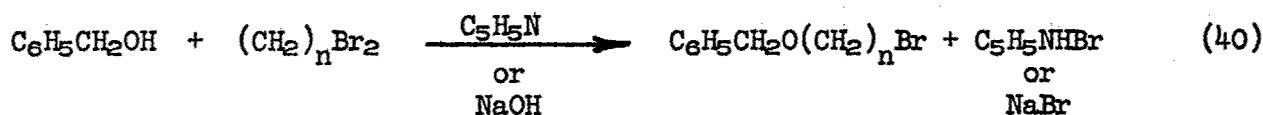
Chlorination of neopentane at -10 to 10°C. following the method of Whitmore<sup>22</sup> gave a 32.3% yield of neopentyl chloride.

### b. Preparation of 1-Chloro-2-benzyloxyethane

To prepare a hydroxyalkyl-substituted triborophane for use in forming a cross-linked polymer, 1-chloro-2-benzyloxyethane<sup>23,24</sup> was prepared in 94% yield by treating 2-benzyloxyethanol with thionyl chloride.

### c. Attempt to Prepare $\alpha$ -Bromomethyl Benzyl Ether and $\beta$ -Bromoethyl Benzyl Ether

In an effort to synthesize a triborophane carrying a P-hydroxyalkyl substituent, two unsuccessful attempts were made to prepare the required bromoalkyl benzyl ether intermediates,  $\alpha$ -bromomethyl benzyl ether ( $n = 1$ ) and  $\beta$ -bromoethyl benzyl ether ( $n = 2$ ).



### d. Preparation of Low Molecular Weight Polyvinyl Chloride

Low molecular weight polyvinyl chloride was obtained from solution polymerization of vinyl chloride in methylene chloride heated at 87-100°C. for 24 hrs. with a catalytic amount of benzoyl peroxide. Isolation was effected by dissolving the crude product in tetrahydrofuran and precipitating the high molecular weight polymer with methanol to give a yellow viscous residue, after removal of the solvent, with a molecular weight of 555 corresponding to a D.P. of 7.5.

Either irradiating vinyl chloride with ultraviolet light (presumably ineffective with the Pyrex tube) or heating at 75-100°C. for extended periods of time failed to initiate polymerization. Low molecular weight polyvinyl chloride has also been obtained from a laboratory sample of telomer supplied by Escambia Chemical Corporation. Dissolution of the telomer in tetrahydrofuran and fractional precipitation of the high molecular weight



polymer with methanol followed by evaporation of the solvent provided a 47% yield of a viscous liquid telomer having a molecular weight of 458 corresponding to a D.P. of 4.8.

The low molecular weight polyvinyl chloride products will be employed as intermediates for the preparation of polyphosphines for use in borophane polymer synthesis.

e. Preparation of Methylphenylphosphinic Acid

A sample of methylphenylphosphinic acid was prepared by the iodic acid oxidation of methylphenylphosphine and used to confirm the identity of a by-product found in the preparation of 1,3,5-trimethyl-1,3,5-triphenyltri-borophane.

B. Experimental

1. Linear Borophane Polymers

a. Preparation of Linear and  
Cyclic Methyl-n-alkyl- and  
Methylphenylborophane Polymers (1371-87, 71, 76, 83, 90,  
92, 132, 133, 95)

Linear and cyclic borophane polymers were prepared on a small scale from a series of methyl-n-alkyl phosphines ( $C_3-C_8$ ) and from methylphenylphosphine. Each borophane polymer was prepared in essentially the same manner from the previously reported secondary phosphine borines<sup>25</sup> and, accordingly, only a general procedure, rather than specific experimental detail, is described herein.

Approximately 20 g. of the secondary phosphine borine and 20 mole per cent triethylamine was placed in a 43 ml. stainless steel pressure vessel fitted with a pressure gauge and valve. The pressure vessel was then heated to 220°C. and held at that temperature until a constant pressure was established. The vessel was then allowed to cool and hydrogen was bled from the reaction through a liquid nitrogen trap and measured using a wet test meter. Data summarizing the stoichiometry and reaction conditions are listed in Table IX.

The crude borophane polymer mixture was transferred from the bomb with the aid of ether as solvent (except with methylphenylborophane where toluene was used) to an addition funnel which served as the feed reservoir for a rotary molecular still. The solvent was removed on a rotary film evaporator and the mixture was passed through a rotary molecular still at the minimum temperature required to distill the cyclic triborophanes. Each of the crude distillates was purified further by refluxing overnight in ethereal solution with an equal volume of methanol containing approximately 0.1 the weight of the crude distillate of aqueous 12N HCl. The methanolic acid phase was discarded and the ethereal layer was washed four times with water. Solvent was removed on a rotary film evaporator and the triborophane was redistilled



TABLE IX

Preparation of P-Methyl-n-alkyl- and P-Methylphenylborophane Polymers

RCH <sub>3</sub> PH·BH <sub>3</sub>		(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N moles	N/P mole ratio	220°C. Pyrolysis		Product Yields		
R	moles			Time, hrs.	Press., psig	H <sub>2</sub> , moles	(Per cent)	Mixed [RCH <sub>3</sub> PBH <sub>2</sub> ] <sub>n</sub> , g. (a)
C <sub>3</sub> H <sub>7</sub>	0.149	0.0366	0.246	19.8	2550	0.155	(104)	17.5
C <sub>4</sub> H <sub>9</sub>	0.166	0.0465	0.280	23.5	2525	0.149	(90)	20.7
C <sub>5</sub> H <sub>11</sub>	0.149	0.0416	0.279	25.0	2700	0.158	(106)	19.2
C <sub>6</sub> H <sub>13</sub>	0.136	0.0336	0.247	19.5	2400	0.132	(97)	19.8
C <sub>7</sub> H <sub>15</sub>	0.134	0.0336	0.251	8.5 <sup>(b)</sup>	2650	0.129	(96)	21.1
C <sub>8</sub> H <sub>17</sub>	0.121	0.0297	0.246	25.5	2000	0.109	(90)	20.4
C <sub>8</sub> H <sub>17</sub>	0.116	0.026 <sup>(c)</sup>	0.224 <sup>(c)</sup>	25.5	3100	0.100	(86)	25.1
C <sub>6</sub> H <sub>5</sub>	0.167	0.0416	0.249	13.0	2000	0.168	(101)	26.0

(a) Crude mixtures still containing much of the excess base.

(b) Minimum time; actual time unknown due to power failure.

(c) Excess methyloctylphosphine used instead of triethylamine.



through a rotary molecular still. Each of the cyclic triborophanes was a mobile liquid at room temperature except 1,3,5-trimethyl-1,3,5-triphenyltriborophane, which was a waxy crystalline solid. Pertinent data are listed in Table X.

An aliquot (1-2 g.) of each of the residues from the molecular distillation was placed in a tube connected in series with traps at ambient temperature and  $-78^{\circ}\text{C}$ . and heated in an oil bath to  $150^{\circ}\text{C}$ . under high vacuum for 20 hrs. except for the methylheptyl- and methyloctylborophane polymers which were heated to  $170^{\circ}\text{C}$ . for 45 hrs. The weights of residual polymer listed in Table X are calculated from the weight of crude polymer and the weight loss of the aliquots.

An additional small scale run of methyloctylborophane polymer was made substituting methyloctylphosphine in place of triethylamine, to determine the effect on yield and degree of polymerization that the less basic end-group might have. The results are included in Table X.

b. Preparation of P-(3,3-Dimethylcyclotrimethylene)borophane Polymers (1350-73, 1391-20)

An unmeasured quantity of 3,3-dimethylcyclotrimethylene-phosphine and 112.7 cc. (5.029 mmoles) of diborane were condensed into a 75 ml. glass bomb tube, equipped with a double seal-off tip. The sealed tube was allowed to warm to room temperature during 24 hrs. after which 1.26 cc. (0.0561 mmole) of hydrogen and 69.0 cc. (3.08 mmoles) of diborane were removed. The tube was resealed, placed in an oven at  $150-155^{\circ}\text{C}$ . for 66.5 hrs., cooled, and opened to remove 89.5 cc. (4.00 mmoles, 102.4% based on diborane) of hydrogen. The solid in the tube was heated to  $170^{\circ}\text{C}$ . under high vacuum to give 0.3779 g. of sublimate analyzed by vapor phase chromatography and a 0.0655 g. residue. The combined weight of solids obtained corresponds to 3.89 mmoles (99.7% based on diborane) of the borophane monomer. The crude mixture was indicated to consist of 83.2% P-tris(3,3-dimethylcyclotrimethylene)triborophane, 2.0% P-tetrakis(3,3-dimethylcyclotrimethylene)tetraborophane, and 14.8% of P-(3,3-dimethylcyclotrimethylene)borophane polymer.

A portion of the sublimate was crystallized from absolute ethanol and resublimed at  $110^{\circ}\text{C}$ . to obtain pure P-tris(3,3-dimethylcyclotrimethylene)triborophane, m.p.  $164.8-165.2^{\circ}\text{C}$ . Anal. calcd. for  $\text{C}_{15}\text{H}_{36}\text{B}_3\text{P}_3$ : C, 52.70; H, 10.62; M.W. 341.8. Found: C, 52.34; H, 10.52; M.W. 341.2 (Neumayer). A qualitative measure of the thermal stability of the triborophane was given by the observation that the melting point remained unaltered after successive 30 min. heating periods at  $200^{\circ}\text{C}$ .,  $250^{\circ}\text{C}$ ., and  $300^{\circ}\text{C}$ . Similar treatment at  $360^{\circ}\text{C}$ . caused significant degradation.

The 0.0655 g. residue had a molecular weight of 672 (Neumayer, D.P. 5.9) and is presumed to be P-(3,3-dimethylcyclotrimethylene)borophane polymer although the possibility that polymerization may have been accompanied by opening of the tetratomic ring has not been excluded.



TABLE X

Separation of P-Methyl-n-alkyl- and P-Methylphenylborophane Polymers

[RCH <sub>3</sub> PBH <sub>2</sub> ] <sub>n</sub>		Triborophane						Borophane Polymer			
R	Wt., g. (a)	Dist. Temp. °C.	Crude Dist. g.	Dist., g.	Yield, %	M.W. (b)	Crude Dist. Residue g.	Dist. Residue g.	M.W. (c)	D.P.	Yield %
C <sub>3</sub> H <sub>7</sub>	17.5	40	5.0	3.8	25.0	303.1 (305.81)	12.0	3.7	3480	34.1	24.1
C <sub>4</sub> H <sub>9</sub>	20.7	64	9.0	5.4 <sup>(d)</sup>	28.0	339.8 (347.89)	9.6	6.5	3030	26.1	33.2
C <sub>5</sub> H <sub>11</sub>	19.2	80	5.8	4.7	24.3	367.1 (389.97)	12.7	9.5	1770	13.6	48.5
C <sub>6</sub> H <sub>13</sub>	19.8	100	3.5	1.1	5.6	415.5 (432.05)	15.3	11.2	1180	8.2	56.6
C <sub>7</sub> H <sub>15</sub>	21.1	130	6.5	2.8	13.2	462.8 (474.13)	13.1	12.1	757	4.8	56.8
C <sub>8</sub> H <sub>17</sub>	20.4	165	7.4	5.6 <sup>(e)</sup>	26.9	479.7 (516.21)	12.0	11.2	1310	7.6	53.3 <sup>(f)</sup>
C <sub>8</sub> H <sub>17</sub> <sup>(f)</sup>	25.1	165	17.1	14.5	72.6 <sup>(f)</sup>	472.7 (516.21)	2.9	2.4	713	4.1	12.0
C <sub>8</sub> H <sub>5</sub>	26.0	165	12.5	11.0	48.4	407.7 (407.86)	6.3	5.6	848	6.2	24.1

(a) Crude mixtures still containing much of the excess base.

(b) Neumayer in benzene.

(c) Microbullimetric in benzene.

(d) Pour point -75°F.; viscosity 16.9 c.s. at 100°F., 3.05 c.s. at 210°F.

(e) Pour point -75°F.; viscosity 33.3 c.s. at 100°F., 5.85 c.s. at 210°F.; flash point 460°F.

(f) Excess methyloctylphosphine used instead of triethylamine.



c. Thermal Decomposition of  
Linear Borophane Polymers

(1) P-Dimethylborophane Polymer (1388-57)

A 0.6530 g. (8.84 mmoles as monomer) quantity of P-dimethylborophane polymer (D.P. 43) was weighed into a pyrolysis tube which was then sealed to a Dry Ice trap. This apparatus was attached to the vacuum line and heated at 180°C. for 21 hrs. The elimination of hydrogen was followed by collecting it by means of a Sprengel pump. Results of the pyrolysis are shown in Table XI.

After completion of the pyrolysis the contents of the -78°C. trap and the cooled residual polymer were removed and weighed. The crystalline sublimate weighed 0.3172 g. (48.6%) and the residue weighed 0.3182 g. (48.7%). The molecular weight determination of the residual polymer gave erratic results ranging from 3400 to 5600 with an average of 4300 for four measurements.

(2) P-Dimethylborophane and P-Methylethylborophane Polymer Mixtures (1388-53)

(a) In the Presence of Hydrogen Chloride

A 1.3973 g. (15.89 mmoles as monomer) sample of P-methylethylborophane polymer (D.P. 26) and 1.1171 g. (15.12 mmoles as monomer) of P-dimethylborophane polymer (D.P. 43) were weighed into a 10 ml. bomb tube. To the evacuated tube 0.72 cc. (0.0032 mmole) of hydrogen chloride was added and the sealed tube was heated for 24 hrs. at 190°C. During the course of heating the contents of the tube appeared to solidify partially. On cooling, a total of 33.2 cc. of hydrogen and 1.06 cc. of condensable gas (presumably alkylphosphines) were removed. On heating the residual liquid under high vacuum at 120°C. for 1 hr. and then raising the temperature to 220°C. for 10 min., 1.774 g. (70.6%) of solid-liquid distillate was obtained, the composition of which is given in Table XII. The solid polymeric residue (0.727 g., 29%) had a broad melting range (120-150°C.). This material was partly fractionated by refluxing in xylene, filtering off the undissolved residue (0.095 g., m.p. 125-130°C.) and recovering 0.652 g. as a greasy solid with an indefinite melting point, but giving a clear melt at 130°C. This material had a molecular weight (microbullimetric in benzene) of  $1400 \pm 20$ , indicating considerable depolymerization had occurred.

(b) Without Added Reagents

In another similar experiment a mixture of 0.3124 g. (3.55 mmoles as monomer) of P-methylethylborophane polymer (D.P. 26) and 0.2727 g. (3.69 mmoles as monomer) of P-dimethylborophane polymer (D.P. 43) was heated in a sealed evacuated bomb tube for 24 hrs. at 190°C. The observed products were 11.0 cc. of condensable gas and 0.4885 g. (83.5%) of a liquid-solid distillate, the composition of which is given in Table XII. The solid residue from this reaction was not investigated further.



TABLE XI

Gaseous Products from Pyrolysis  
of P-Dimethylborophane Polymer at 180°C.

Time, hrs.	Total Hydrogen Evolved, cc.	Total Condensable <sup>(a)</sup> Gas Evolved, cc.
0.25	0.28	-
1.66	0.28 <sup>(b)</sup>	0.28
3.66	0.47	0.28
4.66	0.47	0.32
21.0	0.47	0.32

(a) Presumed to be dimethylphosphine plus triethylamine.

(b) Gas lost.



TABLE XII

Pyrolysis of Mixtures of Both Linear and Cyclic  
P-Dimethylborophane and P-Methylethylborophane Polymers

Compound	Pyrolysis Temp. (24 hrs.) °C	Per cent Yield of [(CH <sub>3</sub> ) <sub>2</sub> PBH <sub>2</sub> ] <sub>3-n</sub> [CH <sub>3</sub> (C <sub>2</sub> H <sub>5</sub> )PBH <sub>2</sub> ] <sub>n</sub> (n = 0-3)*			
		0	1	2	3
[(CH <sub>3</sub> ) <sub>2</sub> PBH <sub>2</sub> ] <sub>x</sub> + [CH <sub>3</sub> (C <sub>2</sub> H <sub>5</sub> )PBH <sub>2</sub> ] <sub>y</sub> + HCl	190	20.2	28.3	28.2	23.3
[(CH <sub>3</sub> ) <sub>2</sub> PBH <sub>2</sub> ] <sub>x</sub> + [CH <sub>3</sub> (C <sub>2</sub> H <sub>5</sub> )PBH <sub>2</sub> ] <sub>y</sub>	190	19.7	29.5	27.9	22.9
[(CH <sub>3</sub> ) <sub>2</sub> PBH <sub>2</sub> ] <sub>3</sub> + [CH <sub>3</sub> (C <sub>2</sub> H <sub>5</sub> )PBH <sub>2</sub> ] <sub>3</sub>	180 ± 2	46.9	nil	nil	53.1
[(CH <sub>3</sub> ) <sub>2</sub> PBH <sub>2</sub> ] <sub>3</sub> + [CH <sub>3</sub> (C <sub>2</sub> H <sub>5</sub> )PBH <sub>2</sub> ] <sub>3</sub>	310 ± 10	48.4	3.7	1.6	46.3

\* By vapor phase chromatographic analysis.



(3) Attempted Reorganization of  
P-Hexamethyltriborophane and  
1,3,5-Trimethyl-1,3,5-Triethyltriborophane (1388-67)

A mixture of 0.1588 g. (0.602 mmole) of 1,3,5-trimethyl-1,3,5-triethyltriborophane and 0.1095 g. (0.494 mmole) of P-hexamethyltriborophane was heated in a sealed evacuated bomb tube at  $180^{\circ} \pm 2^{\circ}\text{C}$ . (refluxing o-dichlorobenzene) for 24 hrs. Only 1.28 cc. of noncondensable and 0.05 cc. of condensable gases were removed from the cooled tube. Vapor phase chromatographic analysis of the mixture is given in Table XII.

In a second experiment a mixture of 1.390 g. (0.627 mmole) of P-hexamethyltriborophane and 0.1581 g. (0.599 mmole) of 1,3,5-trimethyl-1,3,5-triethyltriborophane was heated for 24 hrs. at  $300\text{--}320^{\circ}\text{C}$ . in a sealed evacuated bomb tube to produce 3.51 cc. of hydrogen, 0.30 cc. of condensable gas, (v.t. at  $-78^{\circ}\text{C}$ . 3.5 mm., presumably an alkylphosphine mixture), and 0.2784 g. (93.7%) of a liquid-solid distillate, the composition of which is given in Table XII.

(4) P-Cyclotetramethylene-  
borophane Polymer (1477-23, 1391-166)

The products, particularly the acetone-insoluble product obtained in the preparation of P-cyclotetramethylenetriborophane<sup>8</sup>, were re-investigated. The molecular weights of the acetone-soluble and insoluble fractions indicated the soluble material to be primarily P-tris(cyclotetramethylene)triborophane (calcd. for  $\text{C}_{12}\text{H}_{30}\text{B}_3\text{P}_3$ : M.W. 299.76; found: M.W. 307.4) and the insoluble material to be composed of higher polymers (M.W. 875).

An unweighed amount of the acetone-insoluble polymer was heated under vacuum at  $130^{\circ}\text{C}$ . to remove the admixed triborophane (characterized by m.p.  $166\text{--}168^{\circ}\text{C}$ . and M.W. 299.5) from the waxy solid residue having a molecular weight 1540 (D.P. 15.4). A 0.5079 g. quantity of this residual polymer was heated under vacuum at  $215 \pm 5^{\circ}\text{C}$ . yielding in a  $0^{\circ}$  trap 0.2372 g. of a colorless solid, m.p.  $148\text{--}162^{\circ}\text{C}$ . (46.7%), and in a  $-78^{\circ}\text{C}$ . trap a small amount of clear liquid shown by infrared analysis to be cyclotetramethylenephosphine. The 0.1473 g. residue was heated further at  $300 \pm 15^{\circ}\text{C}$ . to give a further 0.0907 g. of solid, m.p.  $135\text{--}150^{\circ}\text{C}$ . (total 64.6%), a trace of volatile liquid, and a 0.0400 g. residue. An infrared analysis of the two solid sublimates showed them to be impure P-tris(cyclotetramethylene)triborophane.

(5) P-(3,3-Dimethylcyclotri-  
methylene)borophane Polymer (1391-166)

A 0.0531 g. quantity of 3,3-dimethylcyclotrimethyleneborophane polymer, D.P. = 5.9 (vide supra), was heated under vacuum at  $215 \pm 5^{\circ}\text{C}$ . for 5 hrs. and yielded two solids in the air condenser. The more volatile crystalline sublimate, m.p.  $148\text{--}156^{\circ}\text{C}$ ., weighed 0.0031 g. (5.8%) and the less volatile glassy sublimate, m.p.  $54\text{--}56^{\circ}\text{C}$ ., weighed 0.0167 g. (31.5%). The residue was further sublimed by gentle flaming to yield a further 0.0208 g. of glassy solid, m.p.  $81\text{--}87^{\circ}\text{C}$ . (39.2%). Infrared analyses of the solid products



indicated that the more volatile material is largely P-tris(3,3-dimethylcyclo-trimethylene)triborophane; the two glassy sublimates have essentially the same infrared spectra both of which are very similar to the triborophane spectrum except in the 11-15.5 $\mu$  region.

d. Reaction of Linear Borophane  
Polymers with Hydrogen Chloride

(1) P-Dimethylborophane Polymer (1388-50,60)

A 5.954 g. (80.59 mmoles as monomer) quantity of P-dimethylborophane polymer (D.P. 43) was weighed into a 20 ml. bomb tube and 1.41 cc. of purified hydrogen chloride gas was condensed into the evacuated tube. The sealed bomb tube was heated at  $180 \pm 5^\circ\text{C}$ . for 24 hrs. Initially, considerable bubbling was observed but at the end of the heating period the melt had become extremely viscous. On opening the tube the gaseous products were 26.8 cc. of hydrogen, 3.22 cc. dimethylphosphine and 0.46 cc. of material retained by a  $-78^\circ\text{C}$ . trap. The reaction mixture was sublimed under high vacuum for 2 hrs. at  $150-185^\circ\text{C}$ . to yield 0.8721 g. (14.6%) crystalline sublimate, presumed to be triborophane-tetraborophane mixture. The cooled polymer residue was chipped from the reaction vessel. This material failed to dissolve completely in 200 ml. of refluxing benzene during 18 hrs. but it did dissolve in 150 ml. of refluxing toluene. The clear solution was filtered, solvent evaporated and the resulting powder dried under high vacuum to yield 4.525 g. (76%) of polymer, m.p.  $170-171^\circ\text{C}$ . Determinations of the molecular weight were nonreproducible with five experimental values ranging from 1940 to 5200 (average 3200).

A 4.140 g. (56.0 mmoles as monomer) quantity of the above-treated polymer was retreated in an identical manner with 1.10 cc. of hydrogen chloride for 24 hrs. at  $180^\circ\text{C}$ . The gaseous products of the reaction were accidentally lost but 0.3278 g. (7.9%) of a crystalline material was obtained on sublimation. The polymer residue was accidentally destroyed by fire.

In a second experiment 2.5035 g. (33.88 mmoles as monomer) of P-dimethylborophane polymer (D.P. 43) was treated with 0.56 cc. of hydrogen chloride for 21.0 hrs.  $180^\circ\text{C}$ . producing 16.07 cc. of hydrogen and 33.2 cc. of condensable gas. Heating the residue at  $120-210^\circ\text{C}$ . yielded 0.1984 g. (7.9%) of a crystalline sublimate. Recrystallization of the residual polymer from toluene yielded 2.1391 g. (85%) of product. Molecular weight determinations again were nonreproducible giving four experimental values ranging from 2400 to 4400 (average 3250).

(2) P-Methylethylborophane Polymer (1388-8)

A 1.8041 g. (20.52 mmoles) quantity of P-methylethylborophane polymer (M.W. 2260) and 19.4 cc. (0.867 mmole) of hydrogen chloride were sealed in a 20 ml. bomb tube. This mixture was heated at  $180 \pm 10^\circ\text{C}$ . for 18 hrs. On opening the tube the gaseous contents were accidentally lost. The remaining contents of the tube were heated under high vacuum at  $160-170^\circ\text{C}$ . for 2 hrs. under which conditions 0.110 g. of distillate was collected. The



residue, 1.660 g. (92%), failed to dissolve completely in 60 ml. of refluxing n-hexane. The n-hexane solution was cooled and filtered to yield 1.341 g. of an amorphous white solid, m.p. 113-130°C., M.W. 3530. Physical properties of a film cast from this material showed no significant differences from a film cast from the starting material, i.e., both were fairly brittle.

## 2. Cyclic Borophane Polymers

### a. Characterization of 1,3,5-Tri- methyl-1,3,5-triphenyltriborophane (W-1805-1,8,16)

A cursory investigation of the solubility of 1,3,5-trimethyl-1,3,5-triphenyltriborophane<sup>9</sup> in a series of solvents was carried out in the following manner: A small quantity of the distilled triborophane having a molecular weight of 418 (calcd. 407.9) was weighed into a screw-cap test tube and 0.1 ml. of solvent was added. Additional solvent was added in 0.2 ml. increments and the mixture was shaken on a mechanical shaker for 30 min. after each addition until the solid had dissolved. The tube was then reweighed and the approximate solubility at room temperature was calculated.

Slow crystallization of the triborophane from n-hexane, which appeared to be the best recrystallizing solvent, produced principally two distinctly different types of crystals. The first had the form of hexagonal prisms, m.p. 124-126°C., which tended to grow in radiating clusters as well as singularly. The second had the form of unsymmetrical hexagonal plates, m.p. 79-81°C. Anal. calcd. for  $C_{21}H_{30}B_3P_3$ : C, 61.83; H, 7.41; M.W. 407.9. Found: (m.p. 124-126°C.) C, 62.19; H, 7.81; M.W. 403; (m.p. 79-81°C.) C, 62.19; H, 7.72; M.W. 400.

Also formed in much smaller amount was a third type of crystal, m.p. 118-126°C. (M.W. 406), which was identified as methylphenylphosphinic acid by comparison with an authentic sample. The infrared spectrum of each of these crystals was dissimilar but a composite spectrum of the first two was virtually identical with that of the distilled triborophane.

The solubility in n-hexane of each of the two stereoisomers of 1,3,5-trimethyl-1,3,5-triphenyltriborophane was obtained using approximately 4.0 g. of each crystal form placed in separate 10 ml. screw-cap vials having polyethylene-lined caps. The vials were then filled approximately three-fourths full with solvent and weighed. The caps were then covered with a rubber septum to insure against leakage and the vials were rotated for a minimum of 48 hrs. in a thermostat. The vials were then placed on a shelf in the thermostat to allow the solids to settle. The vials were opened briefly and a portion of clear supernatant solution from each was pipetted quantitatively into separate tared weighing bottles. The weight of saturated solution was determined by difference and then the solution was evaporated to dryness in a stream of nitrogen. The last traces of solvent were removed under vacuum before the weight of solid was determined by difference. The temperature of the thermostat was then raised and the procedure repeated.



b. Preparation of P-Hexaneopentyltriborophane (1157-40)

An approximately 23 mmole sample of crude dineopentylphosphine borine was heated at 200°C. in a sealed bulb for 15 hrs. The by-product hydrogen was inadvertently lost on opening the bulb. The mechanically removed solid was sublimed under high vacuum at bath temperatures up to 190°C. to obtain 4.52 g. of crude product, m.p. 140-180°C. leaving a 0.20 g. residual yellow glass. Four recrystallizations from ethanol gave 1.32 g. (2.35 mmoles, ca. 30% yield) of P-hexaneopentyltriborophane, m.p. 201.5-206°C. Anal. calcd. for  $C_{30}H_{22}B_3P_3$ : C, 64.54; H, 13.00; M.W. 558.3. Found: C, 64.50; H, 12.67; M.W. 557 (Neumayer).

c. Preparation of 1,3,5-Trineopentyl-1,3,5-triphenyltriborophane (W-1805-50,70)

A quantity of neopentylphenylphosphine borine was prepared in a 250 ml. bulb from 3.50 g. (19.4 mmoles) of neopentylphenylphosphine and excess (278 cc., 12.4 mmoles) diborane. After three hours contact at a temperature just about ambient, excess diborane (66.8 cc., 2.98 mmoles) was removed leaving 211 cc. (9.42 mmoles, 97.1%) of diborane in the form of the liquid adduct. The adduct was heated in the sealed bulb for 18 hrs. at 200°C. producing 433 cc. (19.3 mmoles, 99.5%) of hydrogen and a clear, colorless, tacky solid which showed a small quantity of P-H absorption in the infrared spectrum and had a molecular weight 555 (calcd. for  $C_{33}H_{54}B_3P_3$  576.2). The crude product was fractionally crystallized from ethanol to obtain two crystalline solids, m.p. 188-191°C. and 100-104°C. Anal. calcd. for  $C_{33}H_{54}B_3P_3$ : C, 68.79; H, 9.45. M.W. 576.2: Found: (m.p. 188-191°C.) C, 69.33; H, 9.47; M.W. 575 (Neumayer); (m.p. 100-104°C.) C, 69.15; H, 9.40; M.W. 578 (Neumayer).

An attempt was made to prepare 1,3,5-trineopentyl-1,3,5-triphenyltriborophane by pyrolysis of the bis(borine) adduct of 3.4 g. (9.5 mmoles) of sym-dineopentylidiphenylbiphosphine. The adduct was prepared in 26 g. of benzene using 218 cc. (9.73 moles) of diborane during 60 hrs. at ambient temperature after which time air was inadvertently admitted to the bulb. The solvent was removed at room temperature and the residual solid was heated for 72 hrs. at 200°C. producing at this temperature a mixture of solid and liquid which solidified at room temperature. The bulb was opened and 285 cc. (12.7 mmoles) of hydrogen was obtained. Fractional sublimation at temperatures up to 120°C. and infrared analysis of the fractions (2.1 g.) indicated that sym-dineopentylidiphenylbiphosphine (m.p. 109-123°C., M.W. 358) and its bis(borine) adduct volatilized in that order leaving a residue (1.0 g.) which appeared to be sym-dineopentylidiphenylbiphosphine bis(borine) contaminated with B-O compounds.

d. Preparation of 1,3,5-Trimethyl-1,3,5-tris(3-dimethylaminopropyl)triborophane (W-1807-1, 11, 95)

Solid methyl-3-dimethylaminopropylphosphine bis(borine), prepared from 0.5169 g. (3.881 mmoles) of methyl-3-dimethylaminopropylphosphine and 86.6 cc. (3.87 mmoles, absorbed from 114.8 cc.) of diborane, was heated at 190°C. for 17.5 hrs. in a sealed tube. The tube was opened and



87.4 cc. (101%) of hydrogen was obtained together with a clear mobile liquid which on hydrolysis in 8 ml. of 6N hydrochloric acid during 15 hrs. at 107°C. produced 268.9 cc. (103%) of hydrogen.

In a second earlier experiment a 9.6400 g. (599 mmoles) quantity of methyl-3-dimethylaminopropylphosphine bis(borine), prepared from a different sample of methyl-3-dimethylaminopropylphosphine, was heated at 195°C. for 17 hrs. in an evacuated sealed 2000 ml. bulb. The bulb was opened and the noncondensable gas, assumed to be hydrogen only, was collected by means of a Sprengel pump. The 1735 cc. (77.4 mmoles) of hydrogen obtained represented a 129.2% yield. The pyrolysis product, a viscous material which appeared opaque because of suspended solid components, was hydrolyzed with 25 ml. of 8N hydrochloric acid at 85°C. for 5 hrs. in the sealed evacuated bulb. The initially clear solution on standing at 25°C. deposited a white crystalline solid, 1.5554 g. (25.2 mmoles), shown by infrared analysis to be boric acid. After basifying the solution with 100 ml. of 4.2N sodium hydroxide and extraction of the borophane product, the solution was analyzed for boron and found to contain an additional 0.0265 meq. representing a total of 0.0517 meq. (86.3% yield) of boron. The hydrogen formed during the hydrolysis was found to be 2107 cc. (94.1 mmoles), bringing the total from the pyrolysis and hydrolysis to 3842 cc. (171.5 mmoles, 71.6%).

The borophane product was extracted from the basic emulsion with three 100 ml. portions of ether. The ether solution was dried over 30 g. anhydrous sodium sulfate. The viscous yellow liquid residue obtained on removal of the ether by distillation weighed 6.0143 g. (41.5 mmoles) representing an over-all yield of 69.2% monomer,  $(\text{CH}_3)_2\text{NC}_3\text{H}_8(\text{CH}_3)\text{PBH}_2$ . Two molecular weight determinations by the Neumayer method were made, one on a sample of the yellow liquid, the second on a sample after further drying by redissolving in ether and evaporation. Anal. calcd. for  $\text{C}_{18}\text{H}_{51}\text{B}_3\text{P}_3\text{N}_3$ : C, 49.69; H, 11.82; M.W. 435.0. Found: C, 48.62; H, 11.58; M.W., 430, 440 (after further drying).

In a preliminary experiment 0.2392 g. (1.796 mmoles) of methyl-3-dimethylaminopropylphosphine (from the same sample used in the second experiment) and 40.7 ml. (1.815 mmoles) of diborane were condensed into a 25 ml. heavy wall tube which was sealed and heated at 175-180°C. for 19 hrs. On opening the tube, 43.8 cc. (1.958 mmoles, 108.9%) of hydrogen was obtained. Excess aqueous hydrochloric acid was condensed into the tube containing the opaque semi-solid residue and the tube was sealed and heated at 120°C. for 1 hr. The hydrogen formed on hydrolysis was inadvertently lost. The clear aqueous solution in the tube was neutralized with excess sodium hydroxide, and ether was used to extract an oil which separated. Without drying the ether was removed by evaporation under vacuum leaving a high boiling, colorless liquid residue, the molecular weight of which was found to be 361; calcd. for 1,3,5-trimethyl-1,3,5-tris(3-dimethylamino)propyltriborophane, 435. An infrared spectrum of this liquid showed the presence of water which would lower the average molecular weight.



e. Attempt to Prepare a Derivative of  
1,3,5-Trimethyl-1,3,5-tris(3-dimethylamino)propyl-  
triborophane Suitable for Fractional Crystallization

(1) The Borane Derivative (W-1807-36)

Into a 25 ml. tube containing 0.8328 g. (5.743 mmoles) of 1,3,5-trimethyl-1,3,5-tris(3-dimethylaminopropyl)triborophane was condensed 69.0 cc. (3.075 mmoles) of diborane, an 11.8% excess over stoichiometric. On warming to ambient temperature the mixture became a viscous semi-solid which was then heated at 100°C. for one hour. Upon opening the tube, 16.6 cc. (0.740 mmole) of hydrogen was obtained and 14.7 cc. (0.656 mmole) of diborane was recovered. Assuming no decomposition the amount of diborane retained as adduct was calculated by difference to be only 84% of the theoretical quantity. The formation of hydrogen indicates some diborane decomposition did occur and the decomposition products may be complexed with the remaining 16% of the tertiary amino groups.

The principal product, an immobile glassy semi-solid, was transferred from the reaction tube to a sublimation tube with the aid of acetone which was removed under reduced pressure. On heating the residue to 160°C. under high vacuum a liquid distillate rather than a crystalline solid collected on the 0°C. condenser.

(2) The Hydrochloride Derivative (W-1807-26)

Anhydrous hydrogen chloride was bubbled into about 3 ml. of a dry ether solution of 1,3,5-trimethyl-1,3,5-tris(3-dimethylamino)propyl-triborophane in a test tube. A white precipitate which adhered tenaciously to the walls of the tube was formed. Attempts to recrystallize the solid from isopropyl alcohol gave only oils.

(3) The Methyl Iodide Derivative (W-1807-30)

To a 0.1211 g. sample of crude 1,3,5-trimethyl-1,3,5-tris-(3-dimethylaminopropyl)triborophane dissolved in 10 ml. of benzene cooled in an ice bath, 1 ml. of methyl iodide was added. After about one minute a white crystalline solid precipitated and was filtered from the solution. The white crystals turned waxy and then appeared to melt leaving a solid which rapidly became sticky and opaque on the filter suggesting perhaps some solvent had solidified and that in addition the solid product was hygroscopic.

A second sample of 0.1358 g. (0.312 mmole) of the amino-derivative was put in a test tube and at 0°C. an excess (1 ml.) of methyl iodide was added slowly. A violent exothermic reaction occurred, but no loss by spattering of the mixture was observed. The excess methyl iodide was removed under vacuum and the weight of the resulting solid indicated the methyl iodide which had reacted weighed 0.1238 g. (0.936 mmole) corresponding precisely to three moles per mole of the triborophane. Attempts to recrystallize the methiodide derivative from ethanol resulted in formation of a white, sticky,



nonfilterable solid.

(4) The Picrate Derivative (W-1807-34)

A sample of 0.3434 g. of the amino-derivative was dissolved in 10 ml. absolute ethanol and added slowly to 10 ml. saturated picric acid solution in 95% ethanol. A red oil separated from the solution without observable evolution of heat. When the solvent was removed the oil solidified to a yellow mass which was insoluble in water and benzene. The picrate derivative was soluble in ethanol, acetone, dimethylsulfoxide, and N,N'-dimethylformamide, but on addition of water the oil separated again.

(5) The Tetraphenylborohydride Derivative (W-1807-41)

A solution of 1.4548 g. of sodium tetraphenylborohydride in 150 ml. of water was added rapidly to a solution of 0.4640 g. of the amino-derivative in dilute acetic acid. A white precipitate formed along with a voluminous white foam. The precipitate appeared to be colloidal and could neither be filtered easily nor coagulated with sodium chloride. Heating the saline solution changed the material to a sticky mass.

To check the procedure dimethyl-3-chloropropylammonium-tetraphenylborohydride was prepared as a crystalline salt which was easily filterable and was successfully recrystallized from ethanol.

f. Preparation of 1,3,5-Trimethyl-1,3,5-triallyltriborophane (W-1807-47,53,63)

Into a carefully cleaned flask fitted with a Teflon covered stirring bar and containing 1.3828 g. of crude 1,3,5-trimethyl-1,3,5-tris-(3-dimethylaminopropyl)triborophane was added 27 ml. of 0.67M hydrogen peroxide in methanol. The solution was stirred for over 24 hrs. to complete the oxidation, the progress of which was checked periodically by mixing a drop of the solution with two drops of water and one drop of phenolphthalein. When no pink coloration was visible the conversion of amine to amine oxide was considered complete.

The excess hydrogen peroxide was decomposed with about 0.2 g. of platinum suboxide ( $\text{PtO}_2$  treated with  $\text{H}_2$ ) during 24 hrs. at ambient temperature. The slurry was filtered and the solvent was removed at reduced pressure leaving a viscous liquid residue which was heated with stirring at  $90^\circ\text{C}$ . for 1 hr. The infrared spectrum of this material was markedly different from the starting material and had a band at  $1608\text{ cm}^{-1}$  which was assigned to the amine oxide band. The liquid was heated at  $160^\circ\text{C}$ . under high vacuum for 1.5 hrs. and the volatile products were collected in traps in series at ca.  $35^\circ\text{C}$ . and  $-196^\circ\text{C}$ . Fractional condensation and infrared analysis of the liquid trapped at  $-196^\circ\text{C}$ . indicated it to be a mixture of methanol and N,N-dimethylhydroxylamine. An infrared spectrum of the high boiling liquid in the  $35^\circ\text{C}$ . trap showed the presence of  $\text{-C=C-}$  unsaturation at  $1640\text{ cm}^{-1}$  in addition to a weak amine oxide band at  $1608\text{ cm}^{-1}$ . The molecular weight was determined by the Neumayer method to be 330 (calcd. for  $\text{C}_{12}\text{H}_{30}\text{B}_3\text{P}_3$ , 300).



g. Preparation of B-halo-  
substituted Triborophanes

(1) P-Hexamethyl-B-iodotriborophane (1385-51, 1157-1)

Two large-scale preparations of P-hexamethyl-B-iodotriborophane were made and worked up in a manner previously described<sup>26</sup>. P-Hexamethyltriborophane, 3.0081 g. (13.57 mmoles), and N-iodosuccinimide, 3.2080 g. (14.26 mmoles), were stirred in 25 ml. of benzene for 64 hrs. to provide 4.3590 g. of crude product. Sublimation at room temperature removed 0.2865 g. of unreacted P-hexamethyltriborophane and at 40-60°C., P-hexamethyl-B-iodotriborophane, m.p. 77-80°C. was collected. Crystallization from ethanol-water (4:1) gave needles of P-hexamethyl-B-iodotriborophane, m.p. 80-82°C., 0.2940 g. (62%), analyzing 99.8% pure by vapor phase chromatography.

In a second experiment, 10.0622 g. (45.4 mmoles) of P-hexamethyltriborophane and 11.1833 g. (49.7 mmoles) of N-iodosuccinimide in 70 ml. of benzene were stirred at room temperature for 6 hrs. Sublimation at 40-60°C. after the usual work-up, provided 13.861 g. (88%) of P-hexamethyl-B-iodotriborophane, m.p. 76-78°C. Crystallization from ethanol-water provided 10.7683 g. (68%) of material, m.p. 80.5-82°C., which assayed 98.9% by vapor phase chromatography.

Further heating (in vacuo) of the sublimation residue provided at a bath temperature of 90-110°C. 0.009 g. of a new material, m.p. 208-213°C., presumably a higher iodinated derivative.

(2) P-Hexamethyl-B,B'-diiodotriborophane (1385-149)

Under a nitrogen atmosphere, 3.2080 g. (14.26 mmoles) of N-iodosuccinimide was added in small quantities during one hour to a stirred solution of 1.5058 g. (6.79 mmoles) of P-hexamethyltriborophane in 60 ml. of benzene. After addition the red solution was heated under reflux (15 min.), stirred overnight at room temperature and heated again under reflux for one hour which caused a color change to brown and the formation of a brown residue. After removal of the solvent in a stream of nitrogen the brown viscous residue was extracted three times with 30 ml. portions of isohexanes, which on concentration to dryness provided a light brown colored residue. Two triturations with water (10 ml.) containing several crystals of sodium thiosulfate followed by several water washes and drying gave 2.5931 g. of a pale yellow solid. An attempt to resolve the mixture by fractional sublimation in high vacuum at a series of temperatures up to 85°C. failed, although the sublimed product was now colorless. The 2.5226 g. of sublimate was separated by repeated fractional crystallization from ethanol and ethanol-water mixtures into two fractions, the first melting in the range of 94-114°C. and the second melting within the broad range of 45-75°C. The lower melting materials were found by vapor phase chromatographic analysis to be primarily (58-82%) P-hexamethyl-B-iodotriborophane containing varying quantities (16-30%) of P-hexamethyl-B,B'-diiodotriborophane. The 0.5890 g. of higher melting material was recrystallized three times from ethanol-water (5:1) to give 0.3434 g. of white needles, m.p. 114-116°C., analyzing (vapor phase chromatography) 97.0% P-hexamethyl-B,B'-diiodotri-



borophane and 2.9% P-hexamethyl-B-iodotriborophane. Two recrystallizations from isohexanes finally provided 0.1158 g. of pure material, m.p. 118.5-119.5°C. Anal. calcd. for  $C_6H_{22}B_3P_3I_2$ : C, 15.22; H, 4.68; M.W. 473.5. Found: C, 15.25; H, 4.72; M.W., 477 (Neumayer).

(3) Attempt to Prepare P-Hexamethyl-B-hexaiodotriborophane (1385-164)

Employing the method recently reported<sup>10</sup>, 11.3570 g. (44.7 mmoles) of iodine was added in small quantities during 5 hrs. to a boiling solution of 1.5025 g. (6.78 mmoles) of P-hexamethyltriborophane in 20 ml. of ethyl iodide. The solution was refluxed for an additional 3 hrs. whereafter the solvent was removed in a stream of nitrogen from the brown colored solution leaving a black residue. Efforts to purify the material by crystallization from a variety of solvents failed. When subjected to heating up to 55°C. in vacuo excess iodine was readily removed leaving a light brown colored residue. A small portion of this residue after three crystallizations from methanol-water gave a white amorphous solid, m.p. 155-165°, the infrared spectrum of which was similar to that for P-hexamethyl-B,B',B''-tribromotriborophane (expt. 4)<sup>27</sup>. Slow crystallization of the remaining brown residue from 40 ml. ethanol provided 0.8791 g. of a white crystalline solid, m.p. 150-175°, with a molecular weight (Neumayer) of 545.

(4) P-Hexamethyl-B,B'-dibromotriborophane (1157-4, 10; W-1810-44)

To a stirred solution of 10.0090 g. (45.16 mmoles) of P-hexamethyltriborophane in 50 ml. of benzene was added slowly 17.0285 g. (95.67 mmoles) of N-bromosuccinimide. After stirring for 6 hrs. the solution was filtered and the filtrate evaporated to dryness in a stream of nitrogen. Trituration of the resulting solid with water removed the succinimide and left 17.1648 g. of light-yellow product which was dissolved in sufficient benzene to form a saturated solution and was passed in 1 ml. quantities through a preparative vapor phase chromatograph equipped with a silicone grease/fire brick column at a temperature of 270°C. The products were collected separately in traps at -196°C., removed with the aid of benzene and evaporated to dryness under vacuum to give 1.4835 g. of P-hexamethyl-B-bromotriborophane assaying 98.4%, 12.9753 g. of P-hexamethyl-B,B'-dibromotriborophane assaying 99.9% and 1.1547 g. of P-hexamethyl-B,B',B''-tribromotriborophane assaying 96.3%. The total weight of separated products was 15.6135 g. corresponding to a 91.0% recovery.

A 0.4000 g. sample of the dibromo-fraction was sublimed in high vacuum at a bath temperature of 55-80°C. to give a white amorphous solid, m.p. 85-110°C. (softening at 72°C.). Anal. calcd. for  $C_6H_{22}B_3P_3Br_2$ : C, 18.99; H, 5.84; M.W., 379. Found: C, 19.14; H, 5.77; M.W., 392 (Neumayer). The infrared spectrum of the material was similar to that for the previously reported pure isomer<sup>28</sup> with several bands shifted slightly and reduced in intensity. The isomeric mixture was fractionally crystallized from 8 ml. of methanol containing 10 drops of water by allowing the solvent to evaporate slowly at room temperature to the volumes listed below before collecting the precipitates.



Fraction	Approx. Vol. of Solution, ml.	Wt., g.	Softening Point, °C.	Melting Point, °C.	Form
1	10	0.0360	123	127-128.5	Transparent needles
2	7	0.0300	123	126.5-128	Transparent needles
3	5.5	0.0161	96	122-126	Transparent needles
4	4	0.0280	70	119-124	Transparent needles
5	3.5	0.0320	72	73-76	Clusters of opaque needles
6	3	0.0393		71-73.5	Clusters of opaque needles
7	1.5	0.0280	60	68-70	Clusters of opaque needles

(5) P-Hexamethyl-B,B,B',B''-  
tetrabromotriborophane (57W-17-145)

A stirred mixture of 2.1134 g. (11.74 mmoles) of N-bromo-succinimide and 0.6477 g. (2.923 mmoles) of P-hexamethyltriborophane in 50 ml. of benzene was rapidly brought to reflux. After refluxing for 3 hrs. the hot benzene solution was extracted with 50 ml. of water, dried over sodium sulfate, and evaporated to dryness to yield 1.467 g. of crystalline solid. This solid, after six recrystallizations from cyclohexane, yielded 0.065 g. of needles, m.p. 208-209°C. Anal. calcd. for  $C_6H_{20}B_3P_3Br_4$ : C, 13.41; H, 3.75; Br, 59.49; M.W. 537.3. Found: C, 13.15; H, 3.60; M.W. (Neumayer) 549.6. The residual solid isolated from the combined mother liquors of the above recrystallizations had a melting range of 100-160°C.

A previously isolated crystalline material<sup>29</sup> (experiment 4) from the reaction of a 6:1 mixture of elemental bromine and P-hexamethyltriborophane had a melting point 208-210°C. Analysis of the previously reported material (C, 13.82; H, 4.12; Br, 59.00) also approximated the tetrabromo derivative and its infrared spectrum showed no  $BH_2$  deformation absorption at  $9\mu$ .



(6) P-Nonamethyl-B-bromobicyclo-  
[4.4.0]pentaborophane Isomers (1385-131)

A mixture of 0.2390 g. (0.676 mmole) of P-nonamethyl-bicyclo[4.4.0]pentaborophane and 0.1250 g. (0.702 mmole) of N-bromosuccinimide (freshly crystallized from water and air dried) in 5 ml. of benzene was stirred under a nitrogen atmosphere for 7 hrs. at room temperature and allowed to stand overnight. The solvent was evaporated in a stream of nitrogen leaving a viscous semi-solid residue which was triturated with 5 ml. of water converting it to a hard, white solid. This solid was further treated with 15 ml. of water, collected and dried on the Buchner funnel to provide 0.2770 g. of product, m.p. 97-114°C. Additional product (0.0061 g., m.p. 98-120°C.) was recovered from the equipment employed by washing with methanol and precipitation of the product with water. The total yield of crude product was thus 0.2831 g. (97% of theoretical P-nonamethyl-B-bromobicyclo[4.4.0]pentaborophane). The crude product was fractionally crystallized from methanol by allowing the solvent to evaporate slowly at room temperature to the volumes listed below before collecting the precipitates. Fractions 2 and 3 crystallized simultaneously and were separated mechanically.

Fraction	Approx. Vol. of Solution, ml.	Wt., g.	Softening Point, °C.	Melting Point, °C.	Form
1	10	0.0300	135	142-144	Hexagonal crystals
2	8	0.0734	140	143-144	Hexagonal crystals
3	8	0.0165	117	120-122.5	Tufts of needles
4	5	0.0305	111	118-122	Tufts of needles
5	3	0.0118	114	119-140	Hexagonal crystals

Combined fractions 1 and 2 (0.1034 g., 0.239 mmole, 35.4% yield) were dissolved in 8 ml. of hot methanol, crystallized by cooling to -25°C., isolated by filtration, and dried in high vacuum to give 0.0758 g. (0.175 mmole, 25.9%) of pure P-nonamethyl-B-bromobicyclo[4.4.0]pentaborophane, m.p. 143-144.0°C. Anal. calcd. for  $C_9H_{35}B_5P_5Br$ : C, 25.01; H, 8.16. Found: C, 25.11; H, 8.19.

The mother liquor was concentrated to 4 ml. and cooled to -25°C. to provide an additional 0.0171 g. of P-nonamethyl-B-bromobicyclo[4.4.0]pentaborophane, m.p. 142.5-143.5°C. (total yield of 0.0929 g., 0.215 mmole, 31.8%). The infrared spectrum of this isomer was virtually identical with that of the P-nonamethyl-B-iodobicyclo[4.4.0]pentaborophane isomer<sup>12</sup> of m.p. 136-137°C.



Fractions 3 and 4 were combined (0.0470 g., 0.109 mmole, 16.1% yield) and crystallized twice from 3 ml. portions of methanol to provide an analytical sample of P-nonamethyl-B-bromobicyclo[4.4.0]pentaborophane, 0.0128 g., m.p. 123.5-125.0°C. Anal. calcd. for  $C_9H_{35}B_5P_5Br$ : C, 25.01; H, 8.16. Found: C, 25.11; H, 8.08. A mixture melting point of the two isomers (m.p. 143.0-144.0°C. and 123.5-125.0°C.), 104-140°C., precluded the possibility of dimorphism.

The infrared spectrum of the lower melting isomer (m.p. 123.5-125.0°C.) was significantly different from that of the higher melting isomer (m.p. 143-144°C.) and was virtually identical with the spectrum of P-nonamethyl-B-iodobicyclo[4.4.0]pentaborophane isomer<sup>12</sup> of m.p. 147.0-148.5°C.

(7) P-Hexamethyl-poly-B-chloro-triborophanes (1157-3)

To a magnetically stirred solution of 10.0391 g. (45.29 mmoles) of P-hexamethyltriborophane in 60 ml. of carbon tetrachloride was added slowly 18.2022 g. (136.3 mmoles) of N-chlorosuccinimide (freshly recrystallized from benzene). Stirring was continued for 6 hrs. and much of the carbon tetrachloride evaporated due to the exothermic nature of the reaction. More carbon tetrachloride was added to insure solution of the product followed by filtration to remove succinimide. The carbon tetrachloride was removed in a stream of nitrogen and the resulting 11.7256 g. of solid was analyzed by vapor phase chromatography with the following results: 8.86% P-hexamethyl-B,B'-dichlorotriborophane, 45.3% P-hexamethyl-B,B',B''-trichlorotriborophane, 39.3%, P-hexamethyl-B,B,B',B''-tetrachlorotriborophane, 3.33%, P-hexamethyl-B-pentachlorotriborophane and 0.44% of P-hexamethyl-B-hexachlorotriborophane. After fractional sublimation into two volatile parts, an attempt was made to separate the 6.0977 g. of more volatile material into its components by preparative vapor phase chromatography. Only crude fractions contaminated with gross quantities (10-15%) of unknown materials, which had apparently been retained in the instrument, were produced. The less volatile sublimate analyzed as 0.5% b-di-, 21.0% B-tri-, 66.7% B-tetra-, 9.4% B-penta-, and 1.6% B-hexachloro-derivatives of P-hexamethyltriborophane and weighed 2.8943 g.

In the same manner in a second experiment, 10.2850 g. (46.40 mmoles) of P-hexamethyltriborophane and 16.4930 g. (123.5 mmoles) of N-chlorosuccinimide in 100 ml. of carbon tetrachloride produced 12.5586 g. of a mixture consisting of 0.5% P-hexamethyltriborophane and 26.9% B-mono-, 41.4% B-di-, 21.5% B-tri-, 6.8% B-tetra-, 1.5% B-penta-, and 1.4% B-hexachloro-derivatives as determined by vapor phase chromatographic analysis.



h. Preparation of Other B-Substituted  
P-Hexamethyltriborophanes from B-Halo-derivatives

(1) B-Carboxylate Derivatives

(a) P-Hexamethyl-B-formoxytriborophane

[1] Using Silver Formate (1385-126)

A heterogeneous mixture of 0.2422 g. (0.697 mmole) of P-hexamethyl-B-iodotriborophane and 0.2116 g. (1.38 mmole) of silver formate (no assay of purity but odor of formic acid was evident) was heated under reflux in 5 ml. of benzene for 9 hrs. in a nitrogen atmosphere. The inorganic salts were filtered and the filtrate evaporated to dryness in a stream of nitrogen to provide 0.2213 g. of a white solid, m.p. 56.5-69°C. On crystallization from ethanol-water (5:4), the melting point (69-75°C.) of the 0.1568 g. of product was not significantly improved. Vapor phase chromatography confirmed that the material was a mixture consisting of 0.01% P-hexamethyltriborophane, 20.8% P-hexamethyl-B-formoxytriborophane and 79.1% P-hexamethyl-B-iodotriborophane; the infrared spectrum confirmed the presence of the formoxytriborophane displaying carbonyl absorption bands at 1700 and 1715  $\text{cm}^{-1}$ , a B-O-C absorption band at 1060  $\text{cm}^{-1}$  and a formate absorption band at 1220  $\text{cm}^{-1}$ . Dilution of the filtrate with additional water provided fine white needles, 0.0342 g., m.p. 46-47.5°C. Analyzing 93.1% P-hexamethyl-B-formoxytriborophane, 6.6% P-hexamethyl-B-iodotriborophane and 0.3% unknown material of very low volatility. The infrared spectrum showed absorption bands at 2830 (C-H in CHO), 1723 and 1705 (C=O), 1208 (C-O) and 1070  $\text{cm}^{-1}$  (B-O-C).

[2] Using Aqueous N,N-Dimethylformamide (1385-182)

A solution of 0.2013 g. (0.579 mmole) of P-hexamethyl-B-iodotriborophane in 9.0 ml. of dimethylformamide and 1.0 ml. of water was heated at 100-105°C. for 5 hrs. After cooling to room temperature and dilution with 25 ml. of water a white microcrystalline material precipitated from the colorless solution. The mixture was cooled in an ice bath and filtered. Iodide ion was detected in the filtrate by treatment with silver nitrate. The thoroughly water-washed crystals were dried to obtain 0.1033 g. (0.389 mmole, 67.2% yield) of P-hexamethyl-B-formoxytriborophane, m.p. 45.5-46.5°C. (softening at 42°C.) which assayed 99.8% by vapor phase chromatography. The impurity, 0.2% was identified as P-hexamethyltriborophane. An analytical sample was prepared by high vacuum sublimation of this material at 25-40°C., onto a cold finger cooled by ice. Anal. calcd. for  $\text{C}_7\text{H}_{24}\text{B}_3\text{P}_3\text{O}_2$ : C, 31.65; H, 9.11; M.W., 265.6. Found: C, 31.47; H, 9.20; M.W., 266 (Neumayer).

The infrared spectrum showed significant absorption bands at 2840 (C-H in CHO), 1725 and 1703 (C=O), 1208 (C-O) and 1070  $\text{cm}^{-1}$  (B-O-C).



[3] Using Aqueous Formamide (W-1810-11)

To 0.1500 g. (0.432 mmole) of P-hexamethyl-B-iodotriborophane in a 5 ml. heavy-wall tube was added 1.50 ml. of formamide and 0.30 ml. of water. The tube was sealed under vacuum and heated at  $100 \pm 2^\circ\text{C}$ . for 19 hrs. After opening on the vacuum line the noncondensable gas (presumably hydrogen) was removed and measured (2.99 cc., 0.133 mmole). The contents of the tube were removed and diluted with the aid of 10 ml. of water, cooled to  $0^\circ\text{C}$ . and the precipitate was collected and dried. The 0.0793 g. of crude product was primarily microcrystalline needles, m.p.  $45.5-47^\circ\text{C}$ ., which formed on the addition of the water, however, it did contain several small pieces of a white, hard, brittle solid, m.p.  $47-48.5^\circ\text{C}$ ., which analyzed (vapor phase chromatography) 76.8% P-hexamethyl-B-formoxytriborophane, 15.0% P-hexamethyl-B-iodotriborophane and 7.9% unknown. The microcrystalline material analyzed 92.3% P-hexamethyl-B-formoxytriborophane, 1.7% P-hexamethyl-B-iodotriborophane and 5.9% unknown. The yield of product was thus approximately 0.073 g. (0.27 mmole, 63%).

An investigation of the aqueous filtrate confirmed the presence of the co-product, ammonium iodide. On treatment of an aliquot with 5% alcoholic silver nitrate a voluminous precipitate of silver iodide was formed instantaneously. On treatment with concentrated sodium hydroxide a volatile basic gas (presumably ammonia) was detected by means of litmus paper. Conclusive evidence for the presence of the  $\text{NH}_4^+$  ion was obtained from a positive Nessler's Reagent Test<sup>14</sup>.

[4] Using Aqueous Formic Acid (W-1810-16)

In a 5 ml. heavy-wall tube was placed 0.1400 g. (0.403 mmole) of P-hexamethyl-B-iodotriborophane and 1.50 ml. of 90.7% formic acid. The evacuated, sealed tube was heated at  $100 \pm 2^\circ\text{C}$ . for 18 hrs. The iodo-derivative, insoluble in the cold medium formed an insoluble liquid at this elevated temperature which dissolved after heating for 2 hrs. On cooling the tube in an ice-bath, clear crystals deposited on the sides of the tube. The tube was opened on the vacuum line and 1.94 cc. (0.087 mmole) of noncondensable gas (presumably hydrogen) was recovered. The tube contents were washed from the tube and diluted with a total of 10 ml. of water. No precipitate formed or could be induced to form by further dilution and/or cooling or seeding with a crystal of the anticipated product. Concentration of the mixture in a stream of nitrogen left a white crystalline solid wet with a viscous oil. The characteristic odor of phosphine was quite evident. An infrared spectrum of the product confirmed the presence of boric acid contaminated with other ill-defined degradation product.



(b) P-Hexamethyl-B-acetoxytriborophane

[1] Using Silver Acetate (1385-60)

In a 10 ml. flask an inhomogeneous mixture of 0.1050 g. (0.302 mmole) of P-hexamethyl-B-iodotriborophane, 0.1015 g. (0.608 mmole) of silver acetate and 3 ml. of benzene was heated under reflux for 12 hrs., after which the mixture was filtered and the filtrate evaporated to dryness in a stream of nitrogen. The residual white solid darkened on standing. Crystallization from 6 ml. of ethanol-water (1:1) removed most of the brown color. Sublimation at 30-55°C. in high vacuum yielded what appeared to be two fractions, 0.0083 g., m.p. 42-44°C. and 0.0516 g., m.p. 43-45°C. The infrared spectra of the two fractions were identical and displayed characteristic absorption bands at 1700  $\text{cm}^{-1}$  (C=O), 1368  $\text{cm}^{-1}$  ( $\text{CH}_3\text{-C}$ ), and 1050  $\text{cm}^{-1}$  (B-O-C) indicating that a total yield of 0.0599 g. (0.214 mmole, 73%) of P-hexamethyl-B-acetoxytriborophane was obtained. Two crystallizations from ethanol-water (1:1) followed by sublimation at room temperature in high vacuum provided an analytical sample, m.p. 44-45°C. Anal. calcd. for  $\text{C}_8\text{H}_{28}\text{B}_3\text{P}_3\text{O}_2$ : C, 34.35; H, 9.37. Found: C, 34.09; H, 9.06.

[2] Using Sodium Acetate (1385-36)

A mixture of 0.1508 g. (0.502 mmole) of P-hexamethyl-B-bromotriborophane and 0.0826 g. (1.01 mmoles) of anhydrous sodium acetate in 8 ml. of absolute ethanol was heated under reflux for 7 hrs. in a nitrogen atmosphere. Dilution of the mixture at room temperature with 10 ml. of water produced 0.1371 g. (91% recovery) of P-hexamethyl-B-bromotriborophane, m.p. 75-77°C., the mixture melting point of which with starting material was undepressed. The infrared spectrum was similar to that of the starting material with no observable absorption in the carbonyl region.

[3] Using Aqueous N,N-Dimethylacetamide (1385-185,W-1810-1)

To 0.2055 g. (0.591 mmole) of P-hexamethyl-B-iodotriborophane was added 9.0 ml. of dimethylacetamide and 1.0 ml. of water and the mixture was heated to 100-105°C. After approximately one hour the colorless solution took on a dark-yellow color which disappeared after one-half hour to return to an almost colorless solution. The solution was maintained at 100-105°C. for a total of 4 hrs., cooled to room temperature and diluted with 25 ml. of water. All efforts to crystallize the product failed until the solution was seeded with authentic P-hexamethyl-B-acetoxytriborophane obtained from the iodo-derivative and silver acetate, whereupon a flocculent micro-crystalline solid immediately formed. After cooling to 0°C. the product was collected, thoroughly washed with water (the filtrate, treated with 5% alcoholic silver nitrate, gave a voluminous precipitate of silver iodide) and air dried, to provide 0.0401 g. (0.143 mmole; 24.2% yield) of P-hexamethyl-B-acetoxytriborophane, m.p. 45-47°C. Further purification was effected by high vacuum sublimation at a bath temperature of 30-55°C. from which 0.0345 g. of product, m.p. 43.5-45.5°C. was obtained. The mixture melting point with



authentic P-hexamethyl-B-acetoxytriborophane was 43.5-46°C. The infrared spectrum was identical with that of the authentic material.

A second experiment was performed in a closed system in anticipation of increasing the yield of product. To 0.3131 g. (0.901 mmole) of P-hexamethyl-B-iodotriborophane in a 5 ml. heavy-wall tube was added from a syringe 2.0 ml. of dimethylformamide and 0.3 ml. of water. A seal-off tip was attached, the solution degassed in high vacuum and the tube sealed. The solid dissolved easily at  $100 \pm 2^\circ\text{C}$ . at which temperature the tube was heated for 4 hrs. On opening the tube in vacuum the noncondensable gas was measured and identified as 0.07 cc. of methane and 15.63 cc. (0.697 mmole) of hydrogen by combustion over cupric oxide. The solution was diluted and washed from the tube with 10 ml. of water. Crystallization again had to be initiated by the addition of a crystal of the authentic acetoxy-derivative. The product was cooled to  $0^\circ\text{C}$ . and collected to provide 0.0566 g. (0.202 mmole, 22.4% yield) of P-hexamethyl-B-acetoxytriborophane, m.p. 42.5-44.5°C. Definitive characterization was accomplished by observing that the infrared spectrum was identical to that of the material prepared previously.

(c) P-Hexamethyl-B-benzoxytriborophane (1385-105)

In a 25 ml. flask equipped with a condenser and a glass-covered magnetic stirring bar, 0.2057 g. (0.592 mmole) of P-hexamethyl-B-iodotriborophane, 0.2806 g. (1.22 mmoles) of silver benzoate, and 5 ml. of benzene were heated under reflux for 7 hrs. in a nitrogen atmosphere. The resulting mixture was filtered to remove the inorganic salts and the filtrate was concentrated in a stream of argon. The residue, sublimed in high vacuum, gave two products, 0.0031 g., m.p. 112-116°C. (softening at  $106^\circ\text{C}$ .) at a bath temperature of  $30-70^\circ\text{C}$ ., and 0.2005 g., m.p. 72-77°C. (softening at  $66^\circ\text{C}$ .), of P-hexamethyl-B-benzoxytriborophane (99% crude yield) at a bath temperature of  $90-150^\circ\text{C}$ . The first sublimate was identified by infrared analysis as benzoic acid contaminated with a small amount of the second sublimate. Characteristic absorption bands<sup>11</sup> in the infrared spectrum of the P-hexamethyl-B-benzoxytriborophane were observed at  $1690\text{ cm}^{-1}$  (C=O),  $1297$  and  $1127\text{ cm}^{-1}$  (benzoate) and  $1050\text{ cm}^{-1}$  (B-O-C). Two crystallizations of the crude material from ethanol-water (3:2) provided 0.1743 g. (86%) of white needles, m.p. 79.5-81.0°C., found by vapor phase chromatography to be free of impurities. An additional crystallization followed by high vacuum sublimation at  $50-75^\circ\text{C}$ . provided an analytical sample, m.p. 81.0-81.5°C. Anal. calcd. for  $\text{C}_{13}\text{H}_{28}\text{B}_3\text{P}_3\text{O}_2$ : C, 45.69; H, 8.26; M.W. 341.7. Found: C, 45.43; H, 8.04; M.W. 342 (Neumayer).

(d) Attempt to Prepare Bis(P-hexamethyl-B-triborophyl) Adipate (W-1810-22)

An evacuated, sealed tube containing 0.1545 g. (0.445 mmole) of P-hexamethyl-B-iodotriborophane, 0.0330 g. (0.229 mmole) of adipamide and 0.50 ml. of water was heated at  $100 \pm 2^\circ\text{C}$ . for 8 hrs. and at  $150 \pm 5^\circ\text{C}$ . for 15 hrs. The clear solution on cooling deposited a white crystalline solid. On opening the tube at  $-196^\circ\text{C}$ . the excessive pressure of noncondensable gas resulted in inadvertent loss of the gas. The tube contents were diluted with 10 ml. of water and the insoluble material, 0.0053 g.,



m.p. 210-215°C. with evolution of a gas, separated. The infrared spectrum displayed bands characteristic of the triborophane nucleus but significantly different from the starting material in the 1000-650  $\text{cm}^{-1}$  region. A very weak carbonyl absorption band at 1700  $\text{cm}^{-1}$  was observed.

The aqueous filtrate gave silver iodide on treatment with 5% alcoholic silver nitrate and evolved ammonia on basification. When made strongly basic (pH 11) with concentrated sodium hydroxide a fine white precipitate, 0.0230 g., m.p. 67-71°C. (softened at 57°C.), of unknown structure formed. The infrared spectrum differed from that of the starting material by an additional strong absorption band at 1130  $\text{cm}^{-1}$  and numerous changes in the 1000-650  $\text{cm}^{-1}$  region. No carbonyl (ca. 1700  $\text{cm}^{-1}$ ) or B-O-C (1050  $\text{cm}^{-1}$ ) absorption bands were observed.

## (2) B-Aryl- and B-Alkyl-Derivatives

### (a) P-Hexamethyl-B-phenyltriborophane and P-Hexamethyl-B,B'-diphenyltriborophane (1385-39)

In a nitrogen-filled 5 ml. heavy-wall tube containing 0.1544 g. (0.444 mmole) of P-hexamethyl-B-iodotriborophane was added by hypodermic syringe 1.00 ml. (30 mmoles) of 3M phenylmagnesium bromide in diethyl ether. The tube was immediately evacuated at -196°C. and degassed. One milliliter of degassed ether was added and the tube sealed. On warming to room temperature the mixture became homogeneous. The tube was heated at 125  $\pm$  2°C. for 15 hrs., then opened on the vacuum line. No noncondensable gas was observed. After removal of the solvent the tacky brown residue was heated in high vacuum to obtain 0.0179 g. of biphenyl (identified by its infrared spectrum) at a bath temperature of 40-70°C. and 0.0040 g. of crude P-hexamethyl-B-phenyltriborophane at 100-125°C. The latter fraction was found by vapor phase chromatography to be a mixture containing 72% P-hexamethyl-B-phenyltriborophane (0.00967 mmole, 2.2%) and 11% P-hexamethyl-B-iodotriborophane. The infrared spectrum of the mixture confirmed the presence of the P-hexamethyl-B-phenyltriborophane.

Hydrolysis of the sublimation residue with water, followed by a second sublimation, provided 0.0245 g. of a yellow solid at 40-75°C., 0.0610 g. of a white solid at 150-170°C., and 0.0263 g. of a second white solid at 180-200°C. The first and second sublimates decomposed quickly to a yellow material on exposure to air; the third sublimate became brown in color. Since the infrared spectra of the first and second sublimates appeared similar to that for the monophenyl and diphenyl derivatives, they were combined and crystallized twice from ethanol-water (10:1) to yield mats of microcrystalline needles, 0.0112g. (7%) of P-hexamethyl-B,B'-diphenyltriborophane, m.p. 161.5-163°C. The mixture melting point with authentic material<sup>30</sup> was 160.5-162.5°C. Similar crystallization of the third sublimate yielded an additional 0.0033 g. of the diphenyl-derivative raising the total to 0.0145 g. (0.0388 mmoles, 8.7%).



(b) P-Hexamethyl-B-ethyltriborophane (1385-136)

To 1.5256 g. (4.39 mmoles) of P-hexamethyl-B-iodotriborophane in a 5 ml. heavy-wall tube was added 1.50 ml. (1.77 g., 14.3 mmoles) of diethylzinc in vacuo. On warming the sealed tube to room temperature the triborophane dissolved. The tube was heated at  $100 \pm 2^\circ\text{C}$ . for 10 hrs., then opened on the vacuum line and the excess diethylzinc removed (no noncondensable gas was observed). The viscous residue was heated under high vacuum at  $30\text{--}50^\circ\text{C}$ . and the distillate was condensed at  $-78^\circ\text{C}$ . No additional material was obtained at temperatures up to  $100^\circ\text{C}$ . The solid product, 0.9610 g., on warming to room temperature melted to a viscous liquid. Analysis by vapor phase chromatography showed it to be a complex mixture consisting of P-hexamethyltriborophane (46.8%), P-hexamethyl-B-ethyltriborophane (39.3%), P-hexamethyl-B,B'-diethyltriborophane (1.3%), P-hexamethyl-B-iodotriborophane (12.4%) and P-hexamethyl-B,B',B''-triethyltriborophane (0.2%). P-Hexamethyl-B-ethyltriborophane, assaying 99.5% by vapor phase chromatography, 0.0801 g., m.p.  $36.5\text{--}37.0^\circ\text{C}$ ., was obtained only after passing the mixture through a preparative vapor phase chromatograph, cutting the appropriate fraction which was again chromatographed, and finally subliming the product under high vacuum at  $25\text{--}30^\circ\text{C}$ . Anal. calcd. for  $\text{C}_8\text{H}_{28}\text{B}_3\text{P}_3$ : C, 38.48; H, 11.30; M.W., 249.7. Found: C, 38.35; H, 11.16; M.W., 252 (Neumayer). The infrared spectrum displayed absorption bands characteristic of the ethyl group at  $1458\text{ cm}^{-1}$  ( $-\text{CH}_2-$ ) and  $1370\text{ cm}^{-1}$  ( $\text{CH}_3\text{-C}$ ).

(c) P-Hexamethyl-B-polymethyltriborophanes (1157-35,41)

Into a 50 ml. heavy-wall tube was placed 14.7 g. of the mixture consisting of the 12.5586 g. of P-hexamethyl-B-polychlorotriborophanes and the 2.8943 g. of the less volatile sublimed P-hexamethyl-B-polychlorotriborophanes (see Section 2 (g) (7) above).

From the vacuum line 32.4 g. (0.28 mole) of dimethylzinc was added, the tube sealed and heated for 9 hrs. at  $110^\circ\text{C}$ . On opening the tube in vacuo 19.4 g. (0.168 mole) of dimethylzinc was recovered. The residue was then sublimed under high vacuum through a 50 cm. tube leading to a  $-78^\circ\text{C}$ . trap at  $60^\circ\text{C}$ . Approximately 25 cm. of the tube adjacent to the reaction tube was maintained at  $80\text{--}90^\circ\text{C}$ . by means of a heating tape which prevented the sublimate (fraction 2) from condensing except in the 25 cm. region adjacent to the  $-78^\circ\text{C}$ . trap. After maintaining these conditions for 48 hrs., the heating tape was removed and the bath temperature raised to  $125^\circ\text{C}$ . where it was kept for 24 hrs. The sublimate (fraction 3) then condensed in the section adjacent to the reaction tube. The tube was disassembled, the contents of each section removed mechanically and analyzed by vapor phase chromatography with the results shown in Table XIII. The three sublimates were individually preparatively chromatographed and the components were collected in common traps and chromatographically analyzed with the results listed in Table XIII.



TABLE XIII

Separation of P-Hexamethyl-B-polymethyltriborophanes

Fraction	Weight, g.	Per cent Distribution of $(\text{CH}_3)_6\text{P}_3\text{P}_3\text{H}_{6-n}(\text{CH}_3)_n$ for Values of n						
		0	1	2	3	4	5	6
Fractional Sublimation								
1 <sup>(a)</sup>	0.3647	6.2	40.7	40.3	10.3	2.5		
2	2.1500	0.3	10.1	46.7	26.6	14.1	1.7	0.5
3a <sup>(b)</sup>	3.4730	0.14	7.32	57.6	26.2	8.44	0.2	0.1
3b <sup>(b)</sup>		0.04	1.27	10.9	13.9	30.8	20.9	22.2
Preparative Vapor Phase Chromatographic Separation								
A <sup>(c)</sup>	--	0.05	45.7	0.6	0.1	6.3	47.2	--
B	--	--	0.5	99.3	--	--	--	0.2
C	--	--	0.04	3.4	96.5	--	--	--
D	--	--	0.04	0.2	4.2	95.5	--	--

(a) Material condensed in the  $-78^\circ\text{C}$ . trap.

(b) Fraction 3 appeared to be two components; (a) opaque needles, and (b) transparent spheroids; total weight 3.4730 g.

(c) Mono- and pentamethyl-derivatives were conveniently collected in the same trap and will be separated by fractional sublimation before recrystallization.



(3) Miscellaneous B-Substituted Derivatives

(a) P-Hexamethyl-B-cyanotriborophane (1157-7)

A larger quantity of P-hexamethyl-B-cyanotri-borophane was prepared by the method previously reported<sup>13</sup> utilizing 5.0009 g. (13.78 mmoles) of P-hexamethyl-B-iodotriborophane (assay 95.8%) and 1.4848 g. (30.29 mmoles) of sodium cyanide in 50 ml. of ethanol. There was obtained 3.238 g. (13.13 mmoles, 95.6% yield) of product, m.p. 104-107°C., which was analyzed by vapor phase chromatography as 97.9% P-hexamethyl-B-cyanotri-borophane, 0.2% P-hexamethyltriborophane, 1.6% P-hexamethyl-B-iodotriborophane and 0.3% P-hexamethyl-B,B'-diiodotriborophane.

[1] Attempt to Hydrolyze  
P-Hexamethyl-B-cyanotriborophane

[a] With Sodium Hydroxide (1385-66,71)

Experiment 1. A mixture of 0.1012 g. (0.410 mmole) of P-hexamethyl-B-cyanotriborophane and 1.0 ml. (0.20 g., 5.0 mmoles) of a 20% aqueous sodium hydroxide solution was heated in a 5 ml. evacuated bomb tube at  $110 \pm 5^\circ\text{C}$ . for 18 hrs. Since the solid remaining appeared much like the starting material, the tube was again heated at  $150 \pm 5^\circ\text{C}$ . for 24 hrs. The appearance of a flocculent solid suspended in the aqueous solution suggested that a reaction had occurred. The tube was opened in vacuo; the noncondensable gas was analyzed by combustion over copper oxide and found to consist of 0.04 cc. methane and 3.85 cc. hydrogen. The contents of the tube were removed mechanically with the aid of 10 ml. of water and filtered. The dried 0.1044 g. filter cake was dissolved in 5 ml. of ethanol to which was added 5 ml. of water. On cooling to  $-20^\circ\text{C}$ ., 0.0710 g. (70% recovery) of P-hexamethyl-B-cyanotriborophane, m.p. 108-110°C., was obtained. Acidification of the basic filtrate yielded on long standing 0.0175 g. of silicon dioxide (identified by its infrared spectrum) as the only product.

Experiment 2. In a 5 ml. heavy-wall tube was placed 0.1057 g. (0.429 mmole) of P-hexamethyl-B-cyanotriborophane and 0.5 ml. (2.5 mmoles) of a 20% aqueous solution of sodium hydroxide. To the evacuated tube 0.7 ml. of degassed ethanol was added and the tube was sealed and heated at  $100 \pm 3^\circ\text{C}$ . for 24 hrs. On cooling to room temperature the transparent solution deposited crystalline needles similar in appearance to the starting material. For this reason the tube was reheated at  $150 \pm 5^\circ\text{C}$ . for 20 hrs. On cooling the entire solution crystallized to a solid mass. The tube was opened on the vacuum line and 4.02 cc. of hydrogen was found. After removal of the water and ethanol on the vacuum line the solid residue was removed from the tube mechanically, to give 0.0965 g. (91% recovery) of P-hexamethyl-B-cyanotriborophane, m.p. 107-109°C. The mixture melting point with authentic material was 104-107°C.; no carbonyl absorption was evident in the infrared spectrum which was identical with that of the starting material. The basic solution failed to give a product on acidification with dilute sulfuric acid.



[b] With Hydrochloric Acid (1385-54,61)

A mixture of 0.0591 g. (0.240 mmole) of P-hexamethyl-B-cyanotriborophane in 3 ml. of concentrated hydrochloric acid was heated under reflux for 5 hrs. The cyanotriborophane, insoluble while cold, was moderately soluble in the refluxing acid. After cooling, 10 ml. of water was added, the solid precipitate was collected, washed thoroughly with water and dried to obtain 0.0272 g. (46% recovery) of crude P-hexamethyl-B-cyanotriborophane, m.p. 96-102°C., definitively characterized by its infrared spectrum. No carbonyl absorption was evident in the infrared spectrum.

In a second experiment, 0.0484 g. (0.105 mmole) of P-hexamethyl-B-cyanotriborophane and 1.0 ml. of concentrated hydrochloric acid were sealed in a 5 ml. heavy-wall tube in vacuo and heated at 150-155°C. for 36 hrs. On opening the tube in vacuo 3.99 cc. of methane and 23.5 cc. (1.05 mmoles, 91%) of hydrogen were measured. The excess hydrochloric acid was removed leaving a white, water soluble residue presumed to be decomposition products of the triborophane ring.

[c] With Sulfuric Acid (1385-56)

A homogeneous solution of 0.0506 g. (0.205 mmole) of P-hexamethyl-B-cyanotriborophane in 2 ml. of acetic acid, 2 ml. of water and 2 ml. of concentrated sulfuric acid was heated under reflux for 3 hrs. No product was obtained upon dilution of the solution with large quantities of water and cooling. Apparently the triborophane nucleus had decomposed under these vigorous conditions.

[d] With Alkaline Hydrogen Peroxide (W-1810-71)

To a well stirred solution of 0.1902 g. (0.771 mmole) of P-hexamethyl-B-cyanotriborophane in 1.0 ml. of absolute ethanol was added 0.40 ml. of 30% hydrogen peroxide followed by 0.10 ml. of 6N sodium hydroxide. No evolution of heat occurred, hence the solution was heated slowly to 50°C. After two hours at this temperature, an additional 0.20 ml. of 30% hydrogen peroxide was added and heating was continued for three additional hours. The solution was cooled to room temperature which resulted in the crystallization of long white needles. After neutralization with 3N sulfuric acid and cooling in an ice bath the solid product was collected, washed with 10 ml. of water, thoroughly dried and identified as 0.1750 g. (92.0%) of starting material, m.p. 108-109°C. Definitive characterization was made by infrared analysis.

[2] Attempts to Reduce P-Hexamethyl-B-cyanotriborophane

[a] With Lithium Aluminum Hydride (W-1810-37)

In a 50 ml. flask equipped with a reflux condenser, nitrogen inlet and outlet and a magnetic stirring bar was



placed 0.3043 g. (1.234 mmoles) of P-hexamethyl-B-cyanotriborophane, 0.1028 g. (2.709 mmoles) of lithium aluminum hydride and 10 ml. of tetrahydrofuran (previously dried over calcium hydride). In a nitrogen atmosphere and with stirring the mixture was heated under reflux for 10 hrs. and then allowed to stand overnight at room temperature. Decomposition of the excess lithium aluminum hydride and reaction products was accomplished by the dropwise addition of 0.5 ml. of water and the resulting residue was separated by filtration. Evaporation of the filtrate to dryness in a stream of nitrogen provided 0.2981 g. of a white amorphous solid residue, m.p. 99-105°C. (softening at 95°C.). Vapor phase chromatographic analysis confirmed that the solid was recovered starting material, P-hexamethyl-B-cyanotriborophane (97.9%) containing P-hexamethyltriborophane (2.1%). The 1.6% P-hexamethyl-B-iodotriborophane and 0.3% P-hexamethyl-B,B'-diiodotriborophane known to be impurities in the starting material apparently had been reduced to P-hexamethyltriborophane.

[b] With Diborane (W-1810-25,32,52)

A 0.1050 g. (0.426 mmole) quantity of P-hexamethyl-B-cyanotriborophane was weighed into a 5 ml. heavy-wall tube. A double seal-off tip was attached, the tube evacuated and 5.86 cc. (0.261 mmole) of diborane added from the vacuum line. The sealed tube was allowed to stand overnight at room temperature with no apparent change, then heated at 105-110°C. for one hour. The resulting colorless viscous oil at room temperature solidified at 0°C. The tube was opened on the vacuum line, 1.54 cc. (0.069 mmole) of hydrogen and a trace amount of diborane were removed. To decompose the reaction product, 0.50 ml. of degassed methanol was added to the tube, the tube was resealed and warmed to room temperature where an effervescence was observed along with solution of the solid. After standing overnight the tube was heated at 100 ± 2°C. for one hour and again opened on the vacuum line. The noncondensable gas, 26.85 cc. (1.198 mmoles), presumably hydrogen, and the excess methanol were removed leaving a white solid residue. Sublimation of the residue from the tube in high vacuum at a bath temperature of 70-105°C. provided 0.0920 g. (0.373 mmole, 87.6% recovery) of starting material, m.p. 101-106°C., which analyzed, by vapor phase chromatography, 99.5% P-hexamethyl-B-cyanotriborophane and 0.5% P-hexamethyltriborophane.

In a second experiment, 0.1121 g. (0.455 mmole) of P-hexamethyl-B-cyanotriborophane, 10.45 cc. (0.466 mmole) of diborane and 0.5 ml. of tetrahydrofuran (dried over sodium) were sealed in a 5 ml. heavy-wall tube under vacuum. Since no visible change appeared to have occurred during two days at ambient temperature hence the tube was heated at 75 ± 2°C. for 4.5 hrs. The tube was opened in vacuum and 3.42 cc. (0.152 mmole) of noncondensable gas (presumably hydrogen), was removed. The material volatile at room temperature was then removed from the tube leaving a clear viscous oil to which was added (at -196°C.) 0.35 ml. of degassed methanol. On warming the sealed tube effervescence was observed. To assure complete decomposition of the product, the tube was heated at 75 ± 2°C. for 1.5 hrs. On opening in vacuum, 41.19 cc. (1.838 mmoles) of hydrogen was removed. After removal of excess methanol there remained a white solid material, 0.1100 g. (0.446 mmole, 98.0% recovery), m.p. 100-106°C. (softening at 93°C.) shown by infrared analysis to be starting material, P-hexamethyl-B-cyanotriborophane.



In a third experiment, 0.1073 g. (0.435 mmole) of P-hexamethyl-B-cyanotriborophane, 9.63 cc. (0.430 mmole) of diborane and 1.5 ml. of pentane (fractionated on the vacuum line by twice condensing it at  $-125^{\circ}\text{C}.$ ) were sealed in a 5 ml. heavy-wall tube and allowed to stand at room temperature for 24 hrs. with occasional shaking. The tube was then opened on the vacuum line at  $-196^{\circ}\text{C}.$  and 1.12 cc. of a noncondensable gas (presumably hydrogen) was removed. Thereafter, all of the material volatile at room temperature was removed and fractionally condensed twice at  $-125^{\circ}\text{C}.$  to recover 3.53 cc. (0.158 mmole) of diborane suggesting 0.272 mmole (126% of theoretical) must have been associated with cyanotriborophane. The white solid residue remaining in the tube was heated in vacuo for 1 hr. at  $200^{\circ}\text{C}.$ , at which temperature the material became a yellow viscous oil. On cooling to room temperature the oil solidified to a yellow mass. The tube was then opened on the vacuum line and 5.72 cc. (0.255 mmole) of noncondensable gas (presumably hydrogen) was removed. The tube was then arranged for high vacuum sublimation through a  $-78^{\circ}\text{C}.$  trap. The sublimate was obtained at a bath temperature of  $60-175^{\circ}\text{C}.$  with only a minor quantity subliming above  $110^{\circ}\text{C}.$  The 0.0420 g. sublimate was found to consist of P-hexamethyltriborophane (26.9%), an unknown (0.6%) and P-hexamethyl-B-cyanotriborophane (72.5%) by vapor phase chromatography. The infrared spectrum confirmed the identity of the major component, P-hexamethyl-B-cyanotriborophane.

The sublimation residue, a yellow oil when hot, solidified to a yellow glass on cooling to room temperature. The residue was heated with 1 ml. of degassed methanol in the sealed tube at  $200 \pm 5^{\circ}\text{C}.$  for 16 hrs. On opening the tube in vacuo 23.92 cc. of a noncondensable gas (presumably hydrogen) was obtained. The methanol was removed leaving a white solid residue which was heated in vacuo to give a white solid sublimate, 0.0106 g., at a bath temperature of  $60-85^{\circ}\text{C}.$  By vapor phase chromatography the sublimate was found to be a mixture of P-hexamethyltriborophane (6.9%), an unknown (0.2%) and P-hexamethyl-B-cyanotriborophane (92.9%). The residual 0.0260 g. of a light-yellow hygroscopic solid which did not melt on sublime up to  $180^{\circ}\text{C}.$ , showed only aliphatic C-H and a B-H absorption at  $2500\text{ cm}^{-1}$ , as readily identified bands on infrared analysis. No evidence of bands normally present in either triborophane or borazene nuclei was observed.

(b) Attempt to Prepare P-Hexamethyl-B-hexacyanotriborophane (1385-155)

To a solution of 0.2527 g. (0.590 mmole) of P-hexamethyl-B-hexachlorotriborophane in 15 ml. of diglyme was added 0.9492 g. (7.09 mmoles) of silver cyanide which was virtually insoluble. The mixture, with continuous stirring, was heated under reflux for 11 hrs. After removing the residual solid from the hot solution and dilution of the filtrate with 10 ml. of water, 0.2037 g. (0.476 mmoles, 80.6%) of P-hexamethyl-B-hexachlorotriborophane, m.p.  $373-375^{\circ}\text{C}.$  (under  $\text{N}_2$ ), was recovered. The infrared spectrum verified the identity of this material and showed no  $\text{C}\equiv\text{N}$  absorption.



(c) P-Hexamethyl-B-iso-  
cyanatotriborophane (1385-97; W-1810-19)

[1] Using Potassium Cyanate

Employing a 50 ml. two-neck flask equipped with a thermometer, magnetic stirring bar and condenser, a heterogeneous mixture of 0.2146 g. (0.617 mmole) of P-hexamethyl-B-iodotriborophane and 0.2000 g. (2.47 mmoles) of potassium cyanate in 10 ml. of dimethylformamide (dried by azeotropic distillation with benzene) was heated at  $100 \pm 5^\circ\text{C}$ . for 8 hrs. The mixture was cooled to room temperature and diluted with 10 ml. of water which effected the precipitation of a white crystalline solid. After cooling to  $-20^\circ\text{C}$ . the precipitate was collected, washed with 5 ml. of water and air dried. There was obtained 0.1380 g. (85% crude yield) of P-hexamethyl-B-iso-cyanatotriborophane, m.p.  $57-63^\circ\text{C}$ . The filtrate, after acidification with nitric acid, gave a yellow precipitate of silver iodide with silver nitrate. Two crystallizations from ethanol-water (5:3) significantly raised the melting point of the product to  $69.5-71.5^\circ\text{C}$ . (0.0931 g., 57%). An additional crystallization afforded even purer material, 0.0803 g., m.p.  $71-72^\circ\text{C}$ . (assaying 99.0% by vapor phase chromatography). The infrared spectrum of this material displayed bands characteristic of the triborophane nucleus and the isocyanato function ( $2280\text{ cm}^{-1}$ ). An analytical sample was prepared by an additional crystallization from ethanol-water (1:1) followed by high vacuum sublimation at  $30-50^\circ\text{C}$ . Anal. calcd. for  $\text{C}_7\text{H}_{23}\text{B}_3\text{P}_3\text{NO}$ : C, 32.01; H, 8.83; M.W., 262.6. Found: C, 32.42; H, 9.03; M.W., 270 (Neumayer).

In a second experiment, 1.0044 g. (2.890 mmoles) of P-hexamethyl-B-iodotriborophane, 0.9448 g. (11.65 mmoles) of potassium cyanate and 20 ml. of dimethylformamide (distilled from calcium hydride) were heated at  $100 \pm 3^\circ\text{C}$ . for 7 hrs. The fine, white solid residue (potassium iodide) was collected after cooling the mixture to room temperature and was found to contain iodide ion by precipitation of silver iodide from an aqueous solution. The filtrate was cooled in an ice bath and slowly diluted with 20 ml. of water. The resulting microcrystalline precipitate was collected and air dried to yield 0.6275 g. (2.39 mmoles, 82.7%) of P-hexamethyl-B-isocyanatotriborophane, m.p.  $71.0-72.5^\circ\text{C}$ ., which assayed 96.6% by vapor phase chromatography. The impurities were P-hexamethyltriborophane, 0.1% (also present in small amount in the starting material) and P-hexamethyl-B-formoxytriborophane, 3.3% resulting from the apparent trace of water in the dimethylformamide (vide supra).

[2] Using Silver Cyanate (1385-166,170)

A heterogeneous mixture of 0.3017 g. (0.868 mmole) of P-hexamethyl-B-iodotriborophane, and 0.1952 g. (1.302 mmoles) of silver cyanate in 10 ml. of benzene was heated at ca.  $50^\circ\text{C}$ . for 1 hr. whereupon the color of the mixture gradually changed from brown to black. The temperature was reduced to approximately  $40^\circ\text{C}$ . and maintained there for 4 hrs. The resulting black residue was removed by filtration and the filtrate evaporated to dryness in a stream of argon. Sublimation under high vacuum provided what appeared to be two materials at a bath temperature of  $40-70^\circ\text{C}$ . The first material formed a hard white solid on the cold finger with the second



forming long white needles on the surface. The two materials were separated mechanically to give 0.1731 g. of the hard solid, m.p. 67-74°C. (softened at 65°C.) which analyzed by vapor phase chromatography as 51.4% P-hexamethyl-B-isocyanatotriborophane, 46.6% P-hexamethyl-B-iodotriborophane, 0.3% P-hexamethyltriborophane and 1.7% unknown materials. The needles, 0.0469 g., m.p. 78-82°C., analyzed 79.7% P-hexamethyl-B-isocyanatotriborophane, 18.9% P-hexamethyl-B-iodotriborophane and 1.3% unknown materials. The calculated quantity of product in these two fractions was thus 0.1264 g. (0.481 mmole), representing a 55.4% yield.

In a second experiment, a heterogeneous mixture of 0.4567 g. (3.05 mmoles) of silver cyanate in a solution of 0.5288 g. (1.521 mmoles) of P-hexamethyl-B-iodotriborophane in 10 ml. of acetonitrile was heated under reflux for 2 hrs. in a nitrogen atmosphere. After heating 1 hr. the mixture darkened and finally turned black. After removal of the black residue attempts to obtain a crystalline product by dilution of the acetonitrile solution with water or evaporation to dryness and crystallization of the residue from aqueous ethanol gave only an orange-red gummy precipitate.

[3] Reaction with Diethylamine.  
P-Hexamethyl-B-(3,3-diethylureido)triborophane (W-1810-58)

To 0.1056 g. (0.402 mmole) of P-hexamethyl-B-isocyanatotriborophane in a 5 ml. heavy-wall tube was added 1.0 ml. of diethylamine in vacuo. On warming the sealed tube to ambient temperature solution was effected. The tube was heated at  $100 \pm 2^\circ\text{C}$ . for 18 hrs., then opened on the vacuum line at  $-196^\circ\text{C}$ . and a small quantity, 1.72 cc., of noncondensable gas, presumably hydrogen, was measured. After removal of the excess diethylamine there remained a white solid residue which was removed mechanically. The 0.1277 g. of crude P-hexamethyl-B-(3,3-diethylureido)triborophane, m.p. 83-89°C., represented a crude yield of 94.6%. Crystallization from 10 ml. of 50% ethanol-water provided 0.0820 g. of fine, white needles, m.p. 97.5-99°C. (softening at 93°C.). Recrystallization from heptane then provided an analytical sample, 0.0264 g., m.p. 101-102°. Anal. calcd. for  $\text{C}_{11}\text{H}_{34}\text{B}_3\text{P}_3\text{N}_2\text{O}$ : C, 39.34; H, 10.21; M.W., 335.8. Found: C, 39.57; H, 10.22; M.W., 395 (Neumayer). Important infrared absorption bands (KBr disc) were present at 3460 (m, N-H), 1628 (vs, C=O), 1493 (vs, N-H bending), 1460 (m, shoulder, -C-CH<sub>2</sub>-) 1428 (m, P-CH<sub>2</sub>), 1413 (m, P-CH<sub>2</sub>), 1373 (m, C-CH<sub>3</sub> symmetrical), 1300 (m, P-CH<sub>3</sub>) and 1285 (P-CH<sub>3</sub>)  $\text{cm}^{-1}$ .

[4] Reaction with Phenol (W-1810-41,43)

A solution of 0.1081 g. (0.412 mmole) of P-hexamethyl-B-isocyanatotriborophane and 0.0680 g. (0.723 mmole) of phenol in a 5 ml. heavy-wall tube sealed under vacuo was heated for 16 hrs. at  $105 \pm 5^\circ\text{C}$ . After opening the tube in vacuo, the phenol, 0.0612 g. (90.0% recovery), was sublimed at room temperature. The residue, 0.1086 g. (100.5% recovery), m.p. 70-71.5°C., was definitively characterized as starting material, P-hexamethyl-B-isocyanatotriborophane, by its infrared spectrum.



In a second experiment, 0.1076 g. (0.410 mmole) of P-hexamethyl-B-isocyanatotriborophane and 0.0676 g. (0.718 mmole) of phenol were heated at 195-200°C. for 6 hrs. A large quantity of noncondensable gas was observed but inadvertently lost on opening the tube. On sublimation of the solid mixture 0.0827 g. of a white crystalline semi-solid sublimate smelling strongly of phenol was obtained at a bath temperature of 60-85°C. On standing in air the phenol volatilized leaving a hard, brittle solid, m.p. 89-94°C. (softening at 85°C.). Crystallization from 4 ml. of ethanol-water (3:1) gave 0.0501 g. of microcrystalline needles, m.p. 89-91°C. (softening at 86°C.) found by vapor chromatography to be a mixture consisting of ca. 45% P-hexamethyl-B-isocyanatotriborophane and 55% P-hexamethyl-B-cyanotriborophane. The infrared spectrum displayed bands characteristic of the two components. Further dilution of the filtrate with water (2 ml.) provided a second product, 0.0100 g., as a white solid, m.p. 102-104°C., found to be ca. 80% P-hexamethyl-B-cyanotriborophane and ca. 20% P-hexamethyl-B-isocyanatotriborophane by vapor chromatography and confirmed by comparison of infrared spectra.

(d) Attempt to Prepare P-hexamethyl-B,B'-diisocyanatotriborophane (W-1810-7)

P-Hexamethyl-B,B'-dibromotriborophane, 0.2050 g. (0.540 mmole), and 0.1750 g. (2.160 mmoles) of potassium cyanate in 8 ml. of absolute ethanol were heated under reflux for 5.5 hrs. The cooled mixture was filtered to remove solids and the filtrate diluted with 8 ml. of water. The resulting 0.1855 g. (90.5% recovery), needle-like precipitate, proved to be P-hexamethyl-B,B'-dibromotriborophane, m.p. 124-125°C., by a mixture melting point (125-127°C.) with authentic material and a direct comparison of its infrared spectrum.

(e) P-Hexamethyl-B-thiocyanotriborophane or P-Hexamethyl-B-isothiocyanatotriborophane (1385-41)

A 50 ml. two-neck flask equipped with a thermometer, glass-covered magnetic stirring bar and a water cooled condenser capped with a nitrogen inlet and outlet was charged with 0.1747 g. (0.503 mmole) of P-hexamethyl-B-iodotriborophane and 0.1500 g. (1.53 mmoles) of potassium thiocyanate, and 8 ml. of dimethylformamide which effected complete solution of the reactants. After heating for 8 hrs. at 100°C. the yellow-colored solution was cooled, and diluted with 20 ml. of water to give an opaque, milky mixture. On cooling at 0°C. overnight the suspension coagulated to give 0.1192 g. (85% crude yield) of product, m.p. 57.5-59°C. The filtrate was acidified with nitric acid and treated with silver nitrate to give a voluminous yellow precipitate of silver iodide.

The infrared spectrum of the crude product displayed a very strong absorption at 2120  $\text{cm}^{-1}$  which in the absence of reference spectra might be interpreted as either the B-thiocyano or B-isothiocyanato derivative of P-hexamethyltriborophane. An analytical sample was prepared by crystallization of the crude material three times from ethanol-water (3:1) to yield white needles, m.p. 63-64°C. Anal. calcd. for  $\text{C}_7\text{H}_{23}\text{B}_3\text{P}_3\text{NS}$ : C, 30.16;



H, 8.32; M.W., 278.7. Found: C, 30.45; H, 8.36; M.W., 282.4 (Neumayer).

(f) P-Hexamethyl-B-mercaptotriborophane (1385-11,14,29)

[1] Using Potassium Hydrosulfide

To a well-stirred solution of potassium hydrosulfide, prepared from 0.0998 g. (1.78 mmoles) of potassium hydroxide in 10 ml. of absolute ethanol, saturated with hydrogen sulfide was added 0.1817 g. (0.523 mmole) of P-hexamethyl-B-iodotriborophane. The solution was heated under reflux for 6 hrs. while maintaining it saturated with hydrogen sulfide by bubbling it into the solution. After cooling and diluting with 15 ml. of water, white needles deposited, 0.1000 g. (98.5%), m.p. 47-50°C. Two crystallizations from ethanol-water (1:1) followed by high vacuum sublimation at 35-41°C. provided an analytical sample of P-hexamethyl-B-mercaptotriborophane, m.p. 50-51°C. Anal. calcd. for  $C_6H_{24}B_3P_3S$ : C, 28.40; H, 9.54. Found: C, 28.12; H, 8.94. The infrared spectrum showed a band at  $2550\text{ cm}^{-1}$  characteristic of the S-H function. Although the melting range and elemental analysis suggested that the product was pure, it was later found to be contaminated with 17.2% P-hexamethyl-B-iodotriborophane by vapor phase chromatography at 250°C. where a slight amount of decomposition was observed as well.

[2] Using Sodium Sulfide

Experiment 1. To 0.2058 g. (0.685 mmole) of P-hexamethyl-B-bromotriborophane and 0.3938 g. (1.64 mmoles) of sodium sulfide nonahydrate in a 5 ml. bomb tube was added 1.5 ml. of dimethylformamide. A seal-off tip was attached to the tube and the contents degassed and sealed under high vacuum. Heating at  $100 \pm 2^\circ\text{C}$ . for 15 hrs. effected almost complete solution; only a small amount of white solid remained. The tube was opened on the vacuum line and the noncondensable gas analyzed and found to contain hydrogen (7.36 cc.) and methane (0.40 cc.). The contents of the tube were removed mechanically with the aid of 4 ml. of dimethylformamide. Addition of 10 ml. of water caused the precipitation of a white flocculent solid, 0.1402 g., m.p. 50.5-52°C. An analytical sample was prepared by an additional crystallization from ethanol-water (3:2) followed by high vacuum sublimation at 25-40°C., m.p. 51.5-52.5°C. Anal. calcd. for  $C_6H_{24}B_3P_3S$ ; M.W., 253.7. Found: 244.3 (Neumayer). Vapor phase chromatography at 250°C. showed only a single major peak representing ca. 99% of the product contaminated only with 0.9% P-hexamethyltriborophane and what appeared to be slightly more volatile decomposition products of the mercapto-derivative. However, the bromo- and mercapto-derivatives are inseparable under these conditions. At a higher column temperature (300°C.) the quantity of decomposition products increased markedly with a corresponding decrease in the quantity of mercapto-compound. The infrared spectrum was similar to that for the P-hexamethyl-B-mercaptotriborophane derived from P-hexamethyl-B-iodotriborophane and potassium hydrosulfide, but with a few minor shifts of absorption bands and poorly resolved band at  $2550\text{ cm}^{-1}$ . A mixture melting point of the mercaptotriborophanes prepared by the two methods was not depressed.



Experiment 2. As in the above experiment, 0.2131 g. (0.709 mmole) of P-hexamethyl-B-bromotriborophane, 0.4012 g. (1.67 mmoles) of sodium sulfide nonahydrate and 2.5 ml. of dimethylformamide were heated at  $100 \pm 2^\circ\text{C}$ . for 12 hrs. The noncondensable gas resulting from the reaction analyzed 0.09 cc. methane and 15.55 cc. hydrogen. The tube contents were treated as above to yield 0.1194 g. of needles analyzing 74.7% P-hexamethyl-B-mercaptotriborophane, 2.0% P-hexamethyltriborophane and 20.3% impurities presumably arising by thermal decomposition at  $300^\circ\text{C}$ . on the chromatographic column. Recrystallization from ethanol-water gave needles, m.p.  $53-54^\circ\text{C}$ . which on admixture with the product from P-hexamethyl-B-iodotriborophane and potassium hydrosulfide had a melting point of  $50-52^\circ\text{C}$ .

(g) P-Hexamethyl-B-methanethiotriborophane (1385-192)

[1] Preparation

A 50 ml. 2-neck flask was equipped with an inlet tube extending to the bottom of the flask, a reflux condenser capped with a nitrogen outlet, and a glass covered magnetic stirring bar. Sodium methanethiolate was prepared under a nitrogen atmosphere by adding 0.4021 g. (8.36 mmoles) of methyl mercaptan beneath the surface of a solution of 0.1348 g. (5.86 mmoles) of sodium in 10 ml. of absolute ethanol maintained at  $0^\circ\text{C}$ . by external cooling. After addition of the methyl mercaptan the inlet tube was removed and 1.0013 g. (2.881 mmoles) of solid P-hexamethyl-B-iodotriborophane was introduced whereafter the opaque solution was heated under reflux for 21 hrs. The solution was filtered to remove a trace quantity of insoluble material and the filtrate was diluted with 5 ml. of water which effected the precipitation of a crystalline solid. The mixture was cooled to  $-25^\circ\text{C}$ ., filtered and the product washed with 10 ml. of water to obtain 0.7105 g. (2.654 mmoles; 92.1% yield) of P-hexamethyl-B-methanethiotriborophane, m.p.  $60.0-60.5^\circ\text{C}$ . An aliquot of the filtrate, acidified with dilute nitric acid, boiled to expel excess methyl mercaptan and treated with 5% alcoholic silver nitrate, gave a copious precipitate of silver iodide.

The product, found by vapor phase chromatography to contain no impurity, was sublimed in high vacuum at a bath temperature of  $30-50^\circ\text{C}$ . to provide an analytical sample, m.p.  $60-61^\circ\text{C}$ . Anal. calcd. for  $\text{C}_7\text{H}_{26}\text{B}_3\text{P}_3\text{S}$ : C, 31.40; H, 9.79; M.W., 267.7. Found: C, 31.37; H, 9.81; M.W., 264.

[2] Reaction with Hydrogen Peroxide (W-1810-5)

A solution of 0.2000 g. (0.747 mmole) of P-hexamethyl-B-methanethiotriborophane in 2.0 ml. of glacial acetic acid was cooled in an ice bath and 0.30 ml. (2.6 mmoles) of 30% hydrogen peroxide was added slowly. A yellow color initially developed which slowly disappeared. The solution was heated on the steam bath for 1.5 hrs., cooled in an ice bath and diluted with 8 ml. of water to precipitate 0.0605 g. of a white solid, m.p.  $105.5-107.5^\circ\text{C}$ . (softened at  $103^\circ\text{C}$ .). Five well-defined peaks were observed on vapor phase chromatographic analysis. Only one peak (the most volatile



component) corresponding to P-hexamethyl-B-methanethiotriborophane, 0.5%, could be identified with certainty. The unknown components, in order of their decreasing volatility, were present in 4.3%, 10.5%, 14.7% and 70.0%. The latter component, being the least volatile and more abundant was believed to be the sulfone. In an attempt to separate the major component by preparative vapor phase chromatography the entire sample was lost because of absorption or decomposition on the column. The original filtrate, evaporated to dryness and washed with water, however, provided an additional 0.0135 g. of product, m.p. 106-107.5°C. (softened at 104°C.). The infrared spectrum of this product had two very intense absorption bands at 1093 and 1228  $\text{cm}^{-1}$  not present in the spectrum of the methanethio-derivative. The two intense absorption bands of organic sulfones usually occur in the regions of 1160-1120  $\text{cm}^{-1}$  and 1350-1300  $\text{cm}^{-1}$  while sulfoxides are reported<sup>31</sup> to have a single strong absorption band in the 1060-1020  $\text{cm}^{-1}$  region.

(h) Reduction of P-Hexamethyl-B-bromotriborophane with Lithium Aluminum Hydride (1385-64)

In a nitrogen atmosphere, 0.1660 g. (0.553 mmole) of P-hexamethyl-B-bromotriborophane was heated under reflux for 7 hrs. with 0.0295 g. (0.778 mmole) of lithium aluminum hydride in 10 ml. of anhydrous ether. The reaction mixture was decomposed with water (8 drops) and the solid residue was isolated by filtration using an additional 10 ml. of ether to wash the equipment and residue. The ether was removed slowly (ca. 48 hrs.) in high vacuum from the solution maintained at -78°C. through a -78°C. trap. After removal of the ether, the white solid residue was sublimed into the trap and weighed. The 0.1622 g. of white solid material, m.p. 70-75°C. (softened at 60°C.) was found to contain 14.2% P-hexamethyltriborophane and 85.8% P-hexamethyl-B-bromotriborophane by vapor phase chromatographic analysis. Since the starting material was found to contain 1.0% P-hexamethyltriborophane under identical chromatographic conditions, the reduction reaction occurred to the extent of ca. 13%.

(i) P-Hexamethyl-B-fluorotriborophane (1385-153,179)

In a 5 ml. heavy-wall tube were placed 0.0495 g. (0.193 mmole) of P-hexamethyl-B-chlorotriborophane, 0.0466 g. (0.803 mmole) of potassium fluoride and 2 ml. of sulfur dioxide. On warming the sealed tube to room temperature the triborophane dissolved while the potassium fluoride appeared to be insoluble; no reaction was observed. After heating overnight at  $80 \pm 2^\circ\text{C}$ . no significant change was apparent but after 80 hrs. at this temperature slight etching of the glass tube was evident. The tube was opened on the vacuum line and the solvent removed leaving a white crystalline residue which was sublimed in high vacuum at 30-60°C. The 0.0431 g. (87.1% recovery), m.p. 67-70°C. (softened at 64°C.) sublimate analyzed by vapor phase chromatography as 1.4% P-hexamethyltriborophane, 94.5% P-hexamethyl-B-chlorotriborophane, and 4.0% P-hexamethyl-B,B'-dichlorotriborophane (essentially the same materials as in the starting material).



In another experiment 0.1132 g. (0.377 mmole) of P-hexamethyl-B-bromotriborophane and 0.0679 g. (1.17 mmoles) of potassium fluoride were placed in a 5 ml. heavy-wall tube and 1.0 ml. of ethylene glycol was added. A seal-off tip was attached and after degassing, the tube was sealed under high vacuum and heated at  $100 \pm 2^\circ\text{C}$ . for 18 hrs. At this temperature a solid phase and two distinct liquid phases were observed. On cooling to room temperature the upper liquid phase solidified to a hard mass. The tube was opened in vacuo and the noncondensable gas (presumably hydrogen), 1.30 cc. (0.058 mmole) was removed. The contents of the tube were diluted with 4 ml. of water, filtered and the residue washed with an additional 3 ml. of water. The filtrate gave a small, yet visible precipitate of silver bromide on treatment with 5% alcoholic silver nitrate. The white crystalline product weighed 0.0843 g., m.p.  $69-73^\circ\text{C}$ . (softening at  $57^\circ\text{C}$ .). The crude product was sublimed to remove last traces of water in high vacuum at a bath temperature of  $25-40^\circ\text{C}$ . to obtain 0.0743 g. of a white amorphous solid, m.p.  $70-75^\circ\text{C}$ . (softening at  $66^\circ\text{C}$ .) which on vapor phase chromatographic analysis on a 2 meter silicone grease/Celite column at  $250^\circ\text{C}$ . gave the following products at the indicated retention times: 1.8% P-hexamethyltriborophane, 3.3 min.; 8.6% P-hexamethyl-B-fluorotriborophane, 3.95 min. (tentative assignment based on the relative retention times of P-hexamethyltriborophane and the B-chloro-derivative); 0.3% unknown, 4.7 min.; 1.5% unknown, 7.1 min.; 87.5% P-hexamethyl-B-bromotriborophane, 8.0 min.; 0.3% P-hexamethyl-B,B'-dibromotriborophane, 19.2 min.

(j) Attempt to Prepare P-Hexamethyl-B-ethoxytriborophane (1385-90)

Sodium ethoxide was prepared under nitrogen in a 50 ml. flask equipped with a condenser from 0.1090 g. (4.74 mmoles) of sodium and 10 ml. of absolute ethanol. P-hexamethyl-B-iodotriborophane, 0.3185 g. (0.916 mmole), was added and the clear solution was heated under reflux for 4.5 hrs. After cooling to room temperature the addition of 4 ml. of water caused the precipitation of fine white needles which were collected and washed with additional water. After thorough air drying, there was obtained 0.2535 g. (80% recovery) of P-hexamethyl-B-iodotriborophane, m.p.  $82-83^\circ\text{C}$ ., having an infrared spectrum identical with that of the starting material. The mixture melting point with authentic material was undepressed.

(k) Attempt to Prepare P-Hexamethyl-B[B-(P-hexamethyltriborophyl)]-triborophane (1385-6,15)

To 0.3070 g. (0.883 mmole) of P-hexamethyl-B-iodotriborophane in 15 ml. of dry ether was added 0.3040 g. (10.1 mmoles) of sodium. In a nitrogen atmosphere, the mixture was heated under reflux for 4 hrs., and allowed to stand overnight at room temperature. The excess sodium was decomposed with methanol followed by 20 ml. of water and the solution extracted with three 10-ml. portions of ether. The ethereal extracts were concentrated in a stream of nitrogen to give a micro-crystalline solid, m.p.  $90-92.5^\circ\text{C}$ . Quantitative measurements were lacking since some of the material was inadvertently lost in the purification steps. The infrared spectrum of the crude product, dissimilar to that of the starting material, contained



absorption bands characteristic of a triborophane. Analysis by vapor phase chromatography proved unsuccessful since the major component apparently decomposed on the column and was not eluted. Small quantities of P-hexamethyltriborophane and an unknown material of slightly less volatility were found to be contaminants. The remaining small quantity of material precluded a closer investigation.

In a similar manner, 0.3220 g. (0.926 mmole) of P-hexamethyl-B-iodotriborophane and 0.3500 g. (15.22 mmoles) of sodium in 15 ml. of anhydrous ether were heated under reflux for 12 hrs. After several unsuccessful attempts to fractionally crystallize a product from methanol and/or methanol-water mixtures, the residue was sublimed in high vacuum. P-hexamethyltriborophane, m.p. 86.5-88°C., was obtained at room temperature, an intermediate fraction, m.p. 62-83°C., at a bath temperature of 25-100°C. and a waxy solid which hardened on standing, m.p. 92-95°C., at a bath temperature of 140-160°C. Crystallization of the latter fraction from ethanol-water provided a crystalline solid (ca. 3 mg.), m.p. 96-98°C. The infrared spectrum compared exactly with the spectrum of the product from the preceding experiment.

(1) Attempt to Prepare P-Hexamethyl-B-  
(N-pentamethylborazyl)triborophane (1385-124)

N-Lithiopentamethylborazene was prepared in a 100 ml. septum bottle under nitrogen from 1.8 ml. (1.72 mmoles) of 0.95M ethereal methyllithium and 0.2486 g. (1.650 mmoles) of N-dimethyl-B-trimethylborazene in 4 ml. of anhydrous ether. After methane evolution subsided the mixture was warmed briefly to 40°C. and allowed to stand 0.5 hr. before adding a solution of 0.5780 g. (1.66 mmoles) of P-hexamethyl-B-iodotriborophane in 5 ml. of anhydrous ether from a syringe. No evidence of reaction was apparent. The mixture was heated at 40°C. for 1 hr. and allowed to stand at room temperature for 2 hrs. before removal of the solvent in a stream of dry nitrogen. The residue was extracted with 20 ml. of pentane, filtered, and the filtrate was evaporated to dryness in a stream of dry nitrogen to obtain a white solid residue. Sublimation in high vacuum at a bath temperature of 50-120°C. gave 0.5236 g. (90.6% recovery) of P-hexamethyl-B-iodotriborophane (identified by vapor phase chromatography) with a slight musty odor characteristic of the borazene. A small amount (0.0599 g.) of residue remained from the sublimation which was not volatile up to 200°C. An infrared spectrum of this material offered no information as to its identity.

(m) Reactions of P-Hexamethyltriborophane

[1] With Trimethylaluminum and Iodine (1385-34)

In a 5 ml. heavy-wall tube was placed 0.1635 g. (0.738 mmole) of P-hexamethyltriborophane and 0.0123 g. (0.048 mmole) of crystalline iodine. The tube was evacuated and 1.0 ml. (0.752 g., 10.43 mmoles) of trimethylaluminum was condensed in from the vacuum line. The sealed tube was heated at  $125 \pm 2^\circ\text{C}$ . for 12 hrs. No noncondensable gas was observed when the tube was opened in high vacuum. After removal of the trimethylaluminum the residual white solid was sublimed in high vacuum at a bath temperature up



to 175°C. The white, solid sublimate (0.1577 g.) proved to be a mixture consisting of 96.3% P-hexamethyltriborophane, 2.7% P-hexamethyl-B-methyltriborophane and 1.0% P-hexamethyl-B,B'-dimethyltriborophane by vapor phase chromatographic analysis.

[2] With Aluminum  
and Organic Halides

[a] Methyl Iodide (1385-31)

A 5 ml. heavy-wall tube was charged with 0.2307 g. (1.04 mmoles) of P-hexamethyltriborophane and 0.2697 g. (10.0 mmoles) of aluminum (8 mesh). To the evacuated tube was added 333.8 cc. (14.9 mmoles) of methyl iodide from the vacuum line. The sealed tube was heated at 125°C. for 45 hrs. resulting in the formation of a red-brown residue. A trace quantity of hydrogen and 277.7 cc. (12.4 mmoles) of methyl iodide were obtained upon opening the tube in vacuo. On sublimation in high vacuum, 0.4938 g. of a white solid was obtained at a bath temperature of 75-105°C. An attempted identification of the mixture by vapor phase chromatography was unsuccessful due to its decomposition and/or absorption of the chromatographic column. Infrared analysis showed the presence of P-methyl, BH and reduced quantities of BH<sub>2</sub> absorption but did not provide sufficient information for definitive characterization.

[b] Ethyl Bromide (1385-49)

To 0.2072 g. (0.935 mmole) of P-hexamethyltriborophane and 0.2525 g. (9.36 mmoles) of aluminum (8 mesh) in a 5 ml. bomb tube was added 1.0 ml. (1.46 g., 13.4 mmoles) of degassed ethyl bromide from the vacuum line. The sealed tube was heated at 125 ± 3°C. for 110 hrs., after which it was opened in vacuo. No permanent gas was observed. A white solid residue remained after removal of 0.2050 g. volatile material which sublimed in high vacuum at bath temperatures up to 120°C. Vapor phase chromatographic analysis of the sublimate indicated it to be a mixture of 86.3% (0.1769 g., 0.798 mmole) P-hexamethyltriborophane and 13.7% (0.0281 g., 0.0935 mmole) P-hexamethyl-B-bromotriborophane corresponding to an 85.3% recovery of starting material and a 10.0% yield of the bromo-derivative.

[c] Iodobenzene (1385-38)

A 5 ml. heavy-wall tube was charged with 0.2017 g. (0.910 mmole) of P-hexamethyltriborophane, 0.2428 g. (9.00 mmoles) of aluminum (8 mesh) and 2.6384 g. (12.93 mmoles) of iodobenzene. The evacuated tube was heated at 125 ± 2°C. for 76 hrs. No permanent gas was observed. The volatile components were removed through a -78°C. trap. On warming to room temperature, the iodobenzene melted leaving a white solid which was dissolved in methanol. The solution was evaporated to dryness to yield 0.1108 g. of P-hexamethyltriborophane, m.p. 83-86°C. The reaction tube was arranged for high vacuum sublimation, and an additional 0.0435 g. of P-hexamethyltriborophane, m.p. 83-88.5°C., was obtained at a bath temperature of 40-65°C. The combined quantity of starting material, the identity of which was confirmed by



The reaction mixture was diluted with 500 ml. of water and filtered. The filter cake was sublimed under high vacuum at 80-90°C. to yield 0.823 g. (78% recovery) of starting material, m.p. 87-89°C. (mixture m.p. 88-89°C.).

Experiment 2. To a stirred mixture of 1.966 g. (8.872 mmoles) of P-hexamethyltriborophane 20 ml. of refluxing distilled water, a solution of 0.963 g. (5.9 mmoles) of potassium permanganate in 20 ml. of water was added dropwise during 1 hr. Rapid formation of manganese dioxide was observed. The cooled reaction mixture was filtered and the filtered cake was air dried. Sublimation of the filter cake yielded 1.413 g. (72%) of starting material m.p. 86-88°C. (mixture m.p. 86-88°C.) and 0.093 g. of an oily liquid trapped at 0°C. Analysis of the filtrate showed it to contain 2.27 mmoles of boron as boric acid (calcd. for complete oxidation of the P-hexamethyltriborophane based on  $8 \text{ MnO}_4^-/\text{triborophane}$ : 2.22 mmoles).

[7] With a Picric Acid (1385-133)

To 5.0 ml. of a saturated solution of picric acid in 95% ethanol was added 0.1502 g. (0.678 mmole) of P-hexamethyltriborophane in 2 ml. of 95% ethanol. The mixture formed no precipitate when allowed to stand overnight at room temperature. On cooling to -25°C. the two types of crystals formed were separated mechanically. The long white needles, 0.0460 g., proved to be P-hexamethyltriborophane, m.p. 85-87°C. (mixture melting point with authentic material was undepressed); the dark-yellow plates, 0.1478 g., proved to be picric acid, m.p. 115-119°. On dilution of the filtrate with 5 ml. of water, a second crop (0.0371 g.) of P-hexamethyltriborophane was obtained, m.p. 86-87.5°C. (mixture melting point was undepressed). After further dilution with 5 ml. of water, 0.0010 g., m.p. of 140-143°C. (dec.) of a light-yellow solid precipitated but the small quantity precluded careful examination. The melting point which was higher than either of the reactants, suggests that a complex may have formed in very low yield.

(n) Preliminary Study of the Colored Complexes  
Derived from Triborophanes and Various  
Organometallic Compounds with Tetracyanoethylene

[1] B-Substituted P-Hexamethyltriborophanes (1385-143)

Preliminary qualitative tests were conducted to determine whether triborophanes formed colored complexes with tetracyanoethylene. Each test utilized about 0.2 g. of tetracyanoethylene in 5-10 ml. of methylene chloride to which was added 0.025-0.050 g. of the triborophane. The visually observed colors are listed below:

P-hexamethyltriborophane	- yellow
P-hexamethyl-B-chlorotriborophane	- yellow
P-hexamethyl-B-bromotriborophane	- light yellow
P-hexamethyl-B-iodotriborophane	- yellow-brown
P-hexamethyl-B-cyanotriborophane	- brown
P-hexamethyl-B-hexamethyltriborophane	- yellow-brown



[2] Organometallic Compounds (1385-144)

Preliminary qualitative tests were conducted utilizing 0.05-0.10 g. of tetracyanoethylene in 3-5 ml. of methylene chloride and 0.01-0.02 g. of a series of organometallic compounds to determine whether molecular complexes would form. The following solution colors were observed.

Triphenylphosphine	- dark red
Triphenylantimony	- orange-brown
Triphenylbismuth	- dark orange-brown
Tetraphenyltin	- yellow
Tetramethyltin	- light yellow
Tetravinyltin	- yellow
Tri-(p-chlorophenyl)phosphine	- orange-red
Tri-(p-tolyl)phosphine	- orange-red
Diphenyl-di-(p-biphenyl) silane	- dark pink
Tetra-(p-biphenyl) silane	- light red
n-Dodecyl-tri(n-decyl) silane	- light yellow
Hexamethylborazene	- yellow

(o) Spontaneous Ignition  
Temperatures of Triborophanes (W-1805-55,59)

Spontaneous ignition temperatures were determined for the triborophanes listed in Table VIII by the technique previously described<sup>16</sup> as a measure of relative oxidative stability. Temperatures were measured using a Temco Model PM-1K17 pyrometer (0-425°C. range) and a chromel-alumel 20-gauge thermocouple having a resistance of 3.4 ohms.

3. Phosphine Borines

a. Preparation of 1,3-Trimethylene-P,P'-bis(methylphosphine Borine) (1434-33, 1391-60)

1,3-Trimethylene-P,P'-bis(methylphosphine borine) has not previously been isolated or characterized, although it has been used as an in situ intermediate in earlier experiments<sup>32</sup>. Two separate preparations were made, the larger of which was used as the starting material for the candidate laminating resin, methylsesquimethyleneborophane polymer.

In the first preparation 29.2 g. (0.214 mole) of 1,3-bis(methylphosphino)propane was maintained at 10°C. while diborane was bubbled into the liquid until it was no longer absorbed. Excess diborane was removed from the product by degassing under high vacuum at ambient temperature.

In the second preparation 338 g. (2.48 moles) of 1,3-bis(methylphosphino)propane was treated with an excess of diborane. The degassed 1,3-trimethylene-P,P'-bis(methylphosphine borine) weighed 403.8 g. (2.47 moles, 99.5%) and had the following physical properties: m.p. 28-30°C. (supercools easily),  $d_{25}^{25}$  0.895,  $n_D^{25}$  1.5215, v.t. 3.3 mm. at 150°C. Anal. calcd. for



$C_5H_{20}B_2P_2$ : C, 36.66; H, 12.31; B, 13.21; P, 37.82; M.W., 163.81. Found: C, 34.1; H, 11.2; B, 12.5; P, 37.6; M.W., 166.7.

b. Preparation of Dineopentylphosphine Borine (1157-40)

To an evacuated 1000 ml. bulb containing 4.2 g. (24 mmoles) of dineopentylphosphine was added 292 cc. (13.1 mmoles) of diborane. The sealed bulb was allowed to stand overnight at room temperature before opening to remove excess diborane from the solid adduct. A 0.0993 g. sample of the adduct was recrystallized twice from pentane to obtain an analytical sample, m.p. 55.5-57°C. Anal. calcd. for  $C_{10}H_{26}BP$ : C, 63.85; H, 13.93. Found: C, 63.80; H, 13.57.

c. Preparation of Neopentylphenylphosphine Borine (W-1805-70)

Neopentylphenylphosphine was treated with excess diborane at a temperature just above ambient for three hours. The resulting adduct was observed to have a melting point 28-29°C. Anal. calcd. for  $C_{11}H_{20}BP$ : C, 68.06; H, 10.39. Found: C, 68.37; H, 10.28.

d. Preparation of Methyl-3-dimethylaminopropylphosphine Bis(borine) (W-1807-6,92,99)

Reaction of 0.5694 g. (4.28 mmoles) of methyl-3-dimethylaminopropylphosphine with 95.9 cc. (4.28 mmoles) of diborane quantitatively formed methyl-3-dimethylaminopropylphosphine bis(borine), m.p. 57.2-59.2°C. Anal. calcd. for  $C_6H_{22}B_2PN$ : C, 44.80; H, 13.79; B, 13.45; P, 19.26; N, 8.71; M.W., 160.9. Found: C, 45.05; H, 13.22; B, 13.47; P, 19.1; N, 8.67; M.W., 173 (ebulliometric in benzene), 177 (Neumayer).

In a second larger scale experiment 7213.6 cc. (0.3220 mole) of diborane was absorbed by a magnetically stirred 42.8394 g. (0.3216 mole) quantity of methyl-3-dimethylaminopropylphosphine which initially was cooled to -78°C. and finally heated to 57°C. as the addition was completed. The crystalline product had a melting point 57.5-59.5°C.

In a preliminary experiment, 10.2652 g. (77.1 mmoles) of methyl-3-dimethylaminopropylphosphine (assay 99.2% by VPC) was transferred in vacuo into a 500 ml., 3-neck, round-bottom flask. The flask was fitted with a Dry Ice condenser, a thermometer, and an inlet tube extending below the surface of the solution formed by adding 250 ml. of pentane. An unmeasured excess of diborane was bubbled into the magnetically stirred solution at room temperature and immediate precipitation of a white solid was observed. As the temperature of the system rose to a maximum of 38°C. the solid melted partially to an immiscible mobile semi-solid. When it was evident that diborane was passing through the solution to the flare, the addition was stopped, the system purged with argon, and the mixture degassed under reduced pressure. The solid adduct was isolated by filtration, washed with pentane, and dried under vacuum to obtain 11.9924 g. (74.5 mmoles) of methyl-3-dimethylaminopropylphosphine bis(borine), m.p. 45-47°C.,



representing a 96.6% yield. Three Neumayer molecular weight determinations in benzene gave the values 182, 183, 186 (calcd. for  $C_6H_{22}B_2PN$  160.9).

#### 4. Organophosphines

##### a. Preparation of 1,3-Bis- (methylphosphino)propane (1391-37)

1,3-Bis(methylphosphino)propane was prepared as described previously<sup>17</sup> using the following quantities of reagents: 153 g. (6.66 moles) sodium, 320 g. (6.66 moles) methylphosphine, and 672 g. (3.33 moles) 1,3-dibromopropane. Fractional distillation of the crude product gave 339.3 g. (2.49 moles, 74.8%) of 1,3-bis(methylphosphino)propane, b.p. 72-73°C./19 mm., assaying 100% by vapor phase chromatography.

##### b. Preparation of 3,3-Dimethyl- cyclotrimethylenephosphine (1350-63,67,182; 1391-3)

Sodium phosphinide was prepared in a 185 ml. Pyrex bomb tube, equipped with a double seal-off tip, from 0.9449 g. (41.10 mmoles) of sodium and 9262.2 cc. (41.35 mmoles) of phosphine in 20 ml. of anhydrous ammonia. The hydrogen (99.97% of theoretical) was removed and a 4.7256 g. (20.55 mmoles) quantity of 1,3-dibromo-2,2-dimethylpropane was syringed into the nitrogen-filled bomb tube cooled to -78°C. The evacuated, sealed tube was removed intermittently from the -78°C. bath for just long enough to melt a little of the solidified dibromo-derivative and allow it to react with the sodium phosphinide. As this process was repeated, the ammonia phase solidified at -78°C. and became more and more difficult to melt. This process was continued until there was no longer an evolution of bubbles from the melted lower organic phase. The tube was then cooled to -196°C. and opened on the high vacuum line. No noncondensable gas was observed. The reaction mixture was fractionated on the high vacuum line by slowly passing the reaction products through a series of traps at -78°C., -125 ± 5°C., and -196°C. The -196°C. trap contained phosphine and the -125°C. trap, ammonia as shown by vapor pressure measurements and infrared analyses. The product in the -78°C. trap, 2.0355 g. (19.934 mmoles, 97% crude yield), was distilled through a glass spiral vapor head fractionating column at -47 to -48°C. The distilled 3,3-dimethylcyclotrimethylenephosphine was characterized by infrared analysis, vapor density molecular weight (calcd. 102.1; found 103.1), and by preparation and pyrolysis of the borine adduct (vide supra). From the quantities used for molecular weight determination and infrared analysis and from the diborane absorption (and subsequent hydrogen and borophane polymer formation) of the unweighed portion, the yield of the cyclic secondary phosphine was calculated as 21.5% (0.4499 g., 4.41 mmoles). An attempt to determine the vapor tension as a function of temperature in the range -78° to 25°C. was unsuccessful due to instability toward polymerization.

##### c. Preparation of Methyl-3- dimethylaminopropylphosphine (1391-150, W-1807-73,85)

In a preliminary experiment sodium methylphosphinide was prepared from 6.39 g. (0.2779 mole) of sodium and an equivalent amount of methylphosphine



in about 300 ml. of liquid ammonia in a 5-neck 1000 ml. flask equipped with a stirrer, Dry Ice condenser vented through a mercury bubbler to a flare, gas inlet tube, port for adding solid reagents, and  $-78^{\circ}\text{C}$ . azeotrope head. A 22.0017 g. (0.1392 mole) quantity of 3-dimethylaminopropyl chloride hydrochloride was added (with considerable difficulty due to caking) to a refluxing ammonia solution of sodium methylphosphinide and the by-product methylphosphine was recovered in the azeotrope head. About 200 ml. of n-hexane and 250 ml. of degassed distilled water were added to the stirred reaction flask. The organic layer was withdrawn by pressure siphon, dried over sodium sulfate, and filtered. The hexane was distilled at atmospheric pressure and the residual material was distilled at reduced pressure to yield 11.2524 g. (0.0845 mole; 60.8%) of methyl-3-dimethylaminopropylphosphine, b.p.  $60-65^{\circ}\text{C}/25-30\text{ mm.}$ , which assayed 99.2% by vapor phase chromatography.

In a larger scale experiment, special care was taken to purify the starting materials. Commercially available 3-dimethylaminopropyl chloride hydrochloride was recrystallized twice from isopropanol (distilled from sodium) and dried under high vacuum to give colorless crystals, m.p.  $142-144^{\circ}\text{C}$ ., which analyzed 99.7% by a non-aqueous titration for base. The mechanical difficulties due to caking of this material were eliminated by casting the compound under a nitrogen atmosphere into 6 mm. diameter cylinders which were added to the reaction mixture from a nitrogen-swept tube. The methylphosphine used was assayed by vapor phase chromatography as 99.9% pure.

In essentially the same manner as in the preliminary experiment the reagents, 35.0 g. (1.52 moles) of sodium, 112.7 g. (0.707 mole) of 3-dimethylaminopropyl chloride hydrochloride, and an equivalent amount of methylphosphine in 1.5 l. of liquid ammonia, produced after purification 45.7 g. (0.344 mole, 48.7%) of methyl-3-dimethylaminopropylphosphine, b.p.  $64-67^{\circ}\text{C}/29-30.5\text{ mm.}$ , which was 98.7% pure by vapor phase chromatographic analysis.

In another experiment on the same scale but using sodium phosphinide to prepare the primary phosphine followed by in situ methylation resulted in appreciable quantities of viscous by-product and only 7.4 g. (0.056 mole, 3.9%) of methyl-3-dimethylaminopropylphosphine, b.p.  $65-68.5^{\circ}\text{C}/30\text{ mm.}$

d. Preparation of Methyl- $\beta$ -hydroxyethylphosphine (1361-95, 1391-46)

Following the method of Knuniantz and Sterlin<sup>33</sup> for the preparation of  $\beta$ -hydroxyethylphosphine, methyl- $\beta$ -hydroxyethylphosphine, b.p.  $113-114^{\circ}\text{C}/155\text{ mm.}$ , 60.0 g. (0.652 mole, assay 93.6% by vapor phase chromatography) was prepared in 50% yield from 30 g. (1.3 moles) of sodium and equivalent amounts of methylphosphine and ethylene oxide in liquid ammonia. The product was redistilled on a spinning band fractionating column to give a material, b.p.  $67^{\circ}\text{C}/20\text{ mm.}$ , assaying 98.6% (by VPC).

e. Attempt to Prepare Methyl-2-(benzyloxy)ethylphosphine (1391-73, 134, 196)

Sodium methylphosphinide was prepared from 23.5 g. (1.022 moles)



of sodium and an equivalent amount of methylphosphine in about 1000 ml. of liquid ammonia. Ethylene oxide was bubbled slowly into the reaction mixture until the yellow color was discharged. During 2 hrs. 143.68 g. (1.022 moles) of benzyl chloride was added slowly and the reaction mixture was stirred for an additional 2 hrs. The ammonia was vented to the flare and replaced with 100 ml. of benzene and 500 ml. of degassed distilled water. The organic layer was separated and the aqueous layer was extracted with three 100 ml. portions of benzene. The combined organic solution was dried over sodium sulfate, filtered, and fractionated on a spinning band column at 19 mm. after the solvent was removed at atmospheric pressure. The product was separated into six overlapping broad fractions boiling from 53°C. to 132°C. (171.26 g.). Infrared and vapor phase chromatographic analyses failed to elucidate the nature of the complex mixture other than to establish methyl- $\beta$ -hydroxyethylphosphine as one of major components.

The experiment was repeated using 23.94 g. (1.041 moles) of sodium and 131.8 g. (1.041 moles) of benzyl chloride with the modification that the liquid ammonia was replaced with an equal volume of dry toluene before addition of the benzyl chloride. After addition of the benzyl chloride, the reaction mixture was heated to reflux. The reaction mixture was processed for distillation. The products, isolated as before, were distilled at 10-13 mm. over a 60-127°C. boiling range again without clear-cut fractions (182.69 g.). Infrared analysis showed only this material was similar to that obtained from the first experiment.

In a third experiment, sodium methylphosphinide was prepared from 6.05 g. (0.2631 moles) of sodium and excess methylphosphine and 46.12 g. (0.2703 mole) of 1-chloro-2-benzyloxyethane was added during 20 min. The reaction mixture was stirred for 1 hr. before the ammonia was vented to the flare and replaced with about 150 ml. of dry toluene which was heated to reflux. About 160 ml. of degassed distilled water was added to the now thick dark-orange mixture. The yellow organic layer was isolated and fractionated on a spinning band column to give 13.8 g., b.p. 51-130°C./100 mm. and 37.5 g., b.p. 88-104°C./18-20 mm. The products appeared by infrared analysis to be similar to those obtained from the first two experiments.

f. Attempt to Improve the  
Organophosphine Synthetic  
Process I<sup>18</sup> (1391-116,122)

Sodium phosphinide was prepared by reaction of 2.35 g. (0.1022 mole) of sodium dissolved in 300 ml. of liquid ammonia with an equivalent amount of phosphine in a 5-neck 1000 ml. flask equipped with a stirrer, 250 ml. addition funnel, Dry Ice condenser vented through a mercury bubbler to a flare, a port for sodium introduction, and a gas addition tube which dipped below the liquid surface. A 150 ml. quantity of dried toluene was added to the flask and the ammonia was vented to the flare. During 30 min., 5.6 ml. (0.1022 mole) of methyl bromide was added to the dark-grey slurry, which changed to a very light grey after an additional 15 min. of stirring. Stirring was continued for another 30 min. after which the slurry was cooled to -78°C. and the methylphosphine was condensed in a -196°C. trap. Toluene



was removed from the product by passing it through a  $-78^{\circ}\text{C}$ . trap and through a zinc sulfate trap at  $0^{\circ}\text{C}$ . to remove residual ammonia. Dissolved phosphine in the methylphosphine was removed by passing the mixture through a  $-130^{\circ}\text{C}$ . trap which retained 5-6 ml. of liquid methylphosphine. The product was lost due to mechanical failure before it could be weighed but from the liquid volume the yield was estimated to be 85%. Confirmation of the yield was obtained from the 89.5% yield of by-product sodium bromide.

In another experiment, an attempt to prepare the intermediate sodium phosphinide in toluene at room temperature rather than in liquid ammonia was unsuccessful.

g. Preparation of Tris-  
(dimethylamino)phosphine (1391-40)

A 45.4 ml. (0.520 mole) quantity of phosphorus trichloride was added to 1050 ml. of diethyl ether at  $0^{\circ}\text{C}$ . in a 3000 ml. flask equipped with a stirrer, a gas inlet tube, and a Dry Ice condenser vented through a mercury bubbler. A 140.6 g. (3.12 moles) quantity of dimethylamine was added to the reaction mixture at  $0^{\circ}\text{C}$ . during 2 hrs. The slurry was agitated for an additional hour, and then pressure siphoned into an enclosed sintered glass filter. The flask and the filter cake were washed 3 times with 100 ml. portions of diethyl ether. The ether was stripped from the combined filtrate and washings through a Vigreux column and the product was distilled on a spinning band fractionating column to give 60.5 g. (0.371 mole, 71.3%) of tris(dimethylamino)phosphine, b.p.  $54-56^{\circ}\text{C}/19\text{ mm.}$ , which was characterized by infrared and vapor phase chromatographic analyses.

h. Preparation of Dimethyl-  
aminophenylchlorophosphine (W-1805-26)

To a stirred solution of 100 ml. (131 g., 0.732 mole) phenyldichlorophosphine in 454 g. diethyl ether cooled to  $0^{\circ}\text{C}$ . in a nitrogen-swept, 1000 ml. 3-neck, round-bottom flask fitted with a Dry Ice condenser, stirrer, and gas addition tube, was added 70 g. (1.552 moles) gaseous dimethylamine during 1.5 hrs. The reaction mixture was then warmed to room temperature and filtered under nitrogen to remove dimethylammonium chloride which was washed with three 70 ml. portions of diethyl ether.

Solvent was removed from the ethereal filtrate under vacuum and the residual material was fractionated on a spinning band column at 2 mm. pressure to give: (1) 16.2 g., b.p.  $74-77^{\circ}\text{C}$ .; (2) 4.2 g., b.p.  $77-78^{\circ}\text{C}$ .; (3) 20.0 g., b.p.  $78^{\circ}\text{C}$ .; (4) 35.0 g., b.p.  $78^{\circ}\text{C}$ .; and an 8.3 g. residue. Anal. calcd. for  $\text{C}_8\text{H}_{11}\text{PNCl}$ : Cl, 18.90. Found: Cl, 18.9 (fraction 3). The yield based on fractions 2-4 was 59.2 g. (0.316 mole) or 43%.

i. Attempt to Prepare o-Bis-  
(dimethylamino)phosphinobenzyl Methyl Ether



(1) o-Lithiobenzyl Methyl Ether (1350-167,177;  
1391-94,112,143)

Experiment 1. A 55.9397 g. (0.2782 mole) quantity of o-bromobenzyl methyl ether, 100 ml. of n-pentane, and 20 ml. of diethyl ether was added to a 5-neck flask equipped with a stirrer, addition funnel, thermometer, dry nitrogen inlet, Dry Ice condenser vented through a mercury bubbler, and a port closed by a rubber septum for removing samples. The flask temperature was maintained at -20 to -10°C. A 423 ml. (0.2971 mole) quantity of n-butyllithium solution (7.24% in n-pentane) was added to the stirred mixture during 3 hrs. Two 0.75 ml. aliquots of the reaction mixture were removed and tested for the presence of alkyllithium compounds<sup>34</sup>. The first aliquot which was removed when 95% of the theoretical butyllithium had been added, tested negative and the second sample, removed after the addition was complete tested positive. The mixture of pentane, diethyl ether, and n-butyl bromide was removed from the organolithium compound under aspirator vacuum through a -78°C. trap. When the volatile materials appeared to have been removed, the mixture was allowed to warm slowly to 20°C. at which temperature a very rapid exothermic reaction occurred which raised the temperature to ca. 150°C. in ca. 1 min. and left a dark-brown fluid throughout the apparatus. The contents of the flask were cooled to 0°C. and tested negatively for the presence of organo-metallic compounds<sup>35</sup>. The mixture was discarded.

Experiment 2. The preparation was repeated using 55.9384 g. (0.2782 mole) of o-bromobenzyl methyl ether and 42.3 ml. (0.2971 mole) of n-butyllithium with the modification that the diethyl ether was omitted and the flask temperature was maintained at -30 to -20°C. No exothermic reaction was observed when the volatile part of the mixture was removed. The distillate in the -78°C. trap was analyzed by vapor phase chromatography and found to contain 0.0773 mole of n-butyl bromide (27.8% of theoretical). n-Pentane was added to the flask and an unsuccessful attempt was made to withdraw the liquid through a sintered glass dip stick. This product mixture was used in the attempt to prepare o-bis(dimethylamino)phosphinobenzyl methyl ether (vide infra).

Experiment 3. A 20.137 g. (0.1005 mole) quantity of o-bromobenzyl methyl ether was placed in a 500 ml. 4-neck flask equipped as before and containing 100 ml. of n-pentane and maintained at -40 to 30°C. A 130 ml. quantity of n-butyllithium solution (ca. 0.110 mole in n-pentane) was added during 1 hr. to the reaction mixture which was now a light tan slurry. The temperature of the mixture was raised to -20°C. for 1 hr. and then to 0°C. for 2 hrs. The reaction slurry was poured onto powdered carbon dioxide. When the mixture had warmed to room temperature about 200 ml. of distilled water was added, and the aqueous layer was separated. The organic layer was washed with three 50 ml. portions of water. The combined aqueous layer and extracts were acidified with concentrated hydrochloric acid. The resulting white solid was filtered, washed with distilled water, and dried to give 11.7142 g. (0.0705 mole, 70.2%) of o-(methoxymethyl)benzoic acid, m.p. 95.0-95.8°C. Anal. calcd. for  $C_9H_{10}O_3$ : C, 65.05; H, 6.07; neut. eq., 166.2. Found: C, 65.08; H, 6.09; neut. eq., 166.4. Infrared analysis showed characteristic aromatic ortho-substitution bands. Confirmation of the ortho-substitution was obtained by allowing 3.1787 g. (19.126 mmoles) of the acid dissolved in about 15 ml.



of glacial acetic acid to react with 35 ml. (19.13 mmoles) of 47% hydriodic acid solution under reflux for 3 hrs. The colorless solution was neutralized with a 50% aqueous sodium hydroxide, made just acidic with hydrochloric acid and extracted with three 50 ml. portions of benzene. The combined benzene extracts were washed with 50 ml. of distilled water, dried over sodium sulfate, and evaporated on a rotary evaporator to give a light yellow solid. The solid was twice recrystallized from water to give phthalid, m.p. 72.5-73.5°C., having an infrared spectrum identical to authentic material. The mixture melting point with authentic material (m.p. 72.5-73.5°C.) was 71-73°C.

(2) o-Bis(dimethylamino)phosphino-  
benzyl Methyl Ether (1350-188)

A 20 ml. quantity of diethyl ether was added to the pentane slurry of o-lithiobenzyl methyl ether previously prepared (vide supra) followed by addition of 47.6504 g. (0.3082 mole) quantity of bis(dimethylamino)chlorophosphine during 0.5 hr. The reaction temperature was maintained at -55 to -20°C. The mixture was allowed to warm slowly to 20°C. during 3 hrs. before the excess bis(dimethylamino)chlorophosphine was destroyed by addition of 30 g. (0.624 mole) of dimethylamine at 5-10°C. during 1 hr. The mixture was refluxed for 3 hrs. and pressure siphoned into an enclosed sintered glass filter funnel where the filter cake was washed with four 50 ml. portions of n-pentane. Solvent was removed from the filtrate cooled to 0°C. at reduced pressure and the residual liquid was distilled through a 40 cm. tantalum spiral fractionation column at 3 mm. to give four fractions: (1) 5.7145 g., b.p. 24.5-29.8°C.; (2) 11.1258 g., b.p. 29.8-33°C., (3) 4.4866 g., b.p. 33-37°C., and (4) 11.6980 g., b.p. 37-74°C. Infrared, vapor phase chromatographic, and elemental analyses for phosphorus and nitrogen for each fraction indicated complex mixtures from which no pure component could be isolated or identified.

j. Preparation of Dimethylamino-  
dineopentylphosphine (1157-33)

To 21 g. (0.114 mole) of dimethylaminodichlorophosphine (prepared as previously reported<sup>36</sup>) in a one l. 4-neck flask under a nitrogen atmosphere was added slowly 172 ml. of 1.58 M (0.272 mole) of neopentylmagnesium chloride<sup>37,38</sup> in an ether solution. After addition of 63 ml. of the Grignard solution to the cooled (-63°C.) and well stirred phosphine, the reaction mixture jelled. On raising the temperature to 0°C. and adding 30 ml. of anhydrous ether the jell became mobile and stirring was continued. The remaining 109 ml. Grignard reagent was added dropwise (2 hrs.) and the mixture was stirred for 64 hrs. at room temperature. An additional 31 ml. of 0.255M (0.008 mole) of ethereal Grignard reagent and 80 ml. of triethylamine were added followed by again stirring for 5 days. The reaction mixture was then pressure filtered through a sintered glass funnel under nitrogen and the filter cake was washed with 200 ml. of ether. The solution was fractionated using a 60 cm. spinning band column to give 20.9 g. (0.096 mole, 68%) of crude dimethylaminodineopentylphosphine, collected at 63-70.5°C./5.5-6.0 mm. Anal. calcd. for C<sub>12</sub>H<sub>28</sub>NP: C, 66.32; H, 12.92. Found: C, 55.85; H, 13.15. In spite of the poor elemental analysis, an infrared spectrum showed characteristic neopentyl absorption bands at 1385 (m) and 1365 (s) as well as a strong P-N band at 975 cm<sup>-1</sup>.



k. Preparation of Dimethylamino-neopentylphenylphosphine (W-1805-29,63)

To a magnetically stirred solution of 19.0 g. (0.101 mole) of dimethylaminophenylchlorophosphine and 70 ml. diethyl ether, contained in a 500 ml. nitrogen-swept flask cooled in an ice water bath, and vented through a mercury bubbler, was added dropwise 63 ml. (0.101 mole) of 1.58M ethereal neopentylmagnesium chloride. The resulting slurry was very viscous at room temperature and triethylamine (148 g., 1.46 moles) was added to make the mixture more filterable and compete with the aminophosphine in complexing with magnesium. The slurry was filtered under nitrogen and the solids were washed with three 75 ml. portions of ether. Ether and triethylamine were removed from the filtrate under reduced pressure at room temperature and the residual material was fractionated on a spinning band column at 10 mm. to obtain 8.0 g., b.p. 109-115°C. and 7.4 g., b.p. 115°C. leaving 0.5 g. residue. The 15.4 g. of product corresponded to a yield of approximately 68%, based on the Grignard reagent. Anal. calcd. for  $C_{13}H_{22}PN$ : C, 69.92; H, 9.93. Found: C, 70.33; H, 10.80.

In a second experiment using 33.5 g. (0.179 mole) of dimethylaminochlorophosphine, 0.201 mole of neopentylmagnesium chloride and 36 g. (0.258 mole) of triethylamine, 22 g. (0.098 mole, 55%) of dimethylaminoneopentylphenylphosphine, b.p. 118-121°C./11 mm., was obtained. Anal. calcd. for  $C_{13}H_{22}PN$ : C, 69.92; H, 9.93; N, 6.27. Found: C, 70.38; H, 9.94; N, 6.46.

1. Preparation of Dineopentylchlorophosphine (1157-36)

To 20.9 g. (96.2 mmoles) of dimethylaminodineopentylphosphine in 250 ml. of diethyl ether under a nitrogen atmosphere and cooled with Dry Ice was added with stirring 7.8 g. (214 mmoles) of hydrogen chloride. The filtrate obtained after removal of dimethylammonium chloride was fractionated employing a 60 cm. spinning band column to give 14.9 g. (71.4 mmoles, 74.2%) of crude dineopentylchlorophosphine, b.p. 55-55.5°C./3 mm. Anal. calcd. for  $C_{10}H_{22}PCl$ : Cl, 17.0. Found: Cl, 18.0. The infrared spectrum lacked the P-N absorption band at  $975\text{ cm}^{-1}$  present in the spectrum of the starting material, but otherwise was virtually the same.

m. Preparation of Neopentylphenylchlorophosphine (W-1805-36,66)

To 15.1 g. (68 mmoles) dimethylaminoneopentylphenylphosphine and 150 ml. diethyl ether, contained in a 500 ml. nitrogen-swept flask cooled in a Dry Ice bath, was added 5.7 g. (156 mmoles) of hydrogen chloride during 1.5 hrs. The resulting slurry was filtered under nitrogen at ambient temperature and the solids were washed with three 25 ml. portions of ether. Solvent was removed from the filtrate under vacuum and the residual material was distilled on a spinning band column to obtain 8.6 g. (40 mmoles, 59% yield) of crude neopentylphenylchlorophosphine, b.p. 110-113°C./10 mm. Anal. calcd. for  $C_{11}H_{16}PCl$ : Cl, 16.51. Found: Cl, 14.8.



On hydrolysis for the chlorine analysis a small quantity of water insoluble liquid was observed but the amount was too small for identification. Infrared analysis suggested that some unchanged starting material remained in the product. In the same manner a second preparation was made using the following quantities of reagents: 21.2 g. (95 mmols) of dimethylamino-neopentylphenylphosphine in 80 ml. diethyl ether and 5.7 g. (156 mmols) of hydrogen chloride. Distillation of the product yielded 9.0 g. (42 mmols, 44%) of crude neopentylphenylchlorophosphine, b.p. 114-116°C./11 mm. Anal. calcd. for  $C_{11}H_{16}PCl$ : C, 71.52; H, 7.51; Cl, 16.52. Found: C, 71.20; H, 7.50; Cl, 14.6. Again the low chlorine analysis and the observation of an organic liquid residue on hydrolysis suggests some residual dimethylaminoneopentylphenylphosphine (ca. 10%) contaminated the product.

n. Preparation of Dineopentylphosphine (1157-39)

To 14.4 g. (68.99 mmols) of dineopentylchlorophosphine in 200 ml. of ether at -78°C. under a nitrogen atmosphere was added 0.79 g. (20.95 mmols) of lithium aluminum hydride in 45 ml. of ether over a period of 3 hrs. After completion of the reaction the ether was distilled and replaced with 60 ml. of hexane. The hexane solution was washed twice with 40 ml. of water before fractionation through a 60 cm. spinning band column to give 5 g. (29 mmols, 42%) of crude dineopentylphosphine collected at 60.5-62°C./10 mm. In addition to the expected neopentyl absorptions the infrared spectrum showed an absorption band at 2280  $cm^{-1}$  (P-H).

o. Preparation of Neopentylphenylphosphine (W-1805-42,68)

To 30 ml. of 0.465M ethereal lithium aluminum hydride (14.0 mmols) contained in a 250 ml. nitrogen-swept flask cooled in a Dry Ice bath, was added dropwise a solution of 8.1 g. (38 mmols) of neopentylphenylchlorophosphine and 10 ml. diethyl ether during 1 hr. The resulting slurry was warmed to room temperature with stirring. Ether was then removed under vacuum. A 20 ml. quantity of n-hexane was added, and the slurry was given three 20 ml. water washes. The hexane phase was then distilled on a spinning band column to obtain 5.5 g. (30.3 mmols, 80.3%) of neopentylphenylphosphine, b.p. 94-95°C./10 mm., and a 2.2 g. residue. Infrared analysis showed the expected characteristic absorptions.

Purification of the residue by three crystallizations in ethyl ether gave a white crystalline solid indicated by infrared analysis and Neumayer molecular weight (353; calcd. for  $C_{22}H_{32}P_2$ , 358.5) to be sym-dineopentyl-di-phenylbiphosphine.

In another experiment reversed addition of reagents was used. To 8.2 g. (38 mmols) neopentylphenylchlorophosphine and 100 ml. diethyl ether, contained in a 500 ml., nitrogen-swept flask cooled in a Dry Ice bath, was added 23 ml. of ethereal (0.465M) lithium aluminum hydride (11 moles) during 1 hr. A small quantity of solid which formed, was removed by filtration under nitrogen at ambient temperature and washed with two 10 ml. portions of ether. Solvent was removed from the filtrate under vacuum and the residual material was heated on a spinning band column without distillation up to 190°C. About



100 ml. of hexane was added to dissolve the cooled residual solid. The hexane solution was washed with two 100 ml. portions of water. The solvent was then removed under vacuum and the resulting solids were sublimed at 120°C. to obtain 3.4 g. of solid which had an infrared spectrum virtually identical with that previously obtained for sym-dineopentyldiphenylbiphosphine. The solid, m.p. 119-125°C., had a microbullioscopic molecular weight of 327 in benzene.

p. Preparation of Di-substituted  
Aromatic Phosphorus Compounds

(1) p-Bis(dimethylamino-  
methylphosphino)benzene (1388-33)

To a stirred solution of 0.44 mole of butyllithium in 650 ml. of pentane was added 51.0 g. (0.216 mole) of p-dibromobenzene in 100 ml. of pentane. The stirred reaction mixture was refluxed for 24 hrs. The cooled yellow slurry was filtered and the filter cake washed with two 100 ml. portions of pentane. The bright-yellow powder was reslurried in pentane and added to a rapidly stirred solution of 26.5 g. of methyldimethylaminochlorophosphine in 100 ml. of pentane and 50 ml. of diethyl ether maintained at -60°C. After approximately one-half of the dilithiobenzene slurry had been added the Michler's ketone test was negative; after all the slurry had been added the test was positive. At this time the reaction mixture was allowed to warm to room temperature and stirred 1.5 hrs. The reaction mixture was filtered under nitrogen and the filter cake washed twice with 100 ml. portions of pentane. The combined filtrate and washings were distilled (after removal of pentane) under high vacuum to obtain the following fractions:

Fraction	Temp., °C.	Wt., g.	I.R.	Beilstein Test
1	trapped at -78	4.8	$[(CH_3)_2N]_2PCH_3$	
2	85-95	3.6	Aromatic	+
3	95-110	6.2	Aminophosphines	-
4	110-130	3.7	Aminophosphines	-
5	150-180	2.3	(not taken)	+

Fractions 3 and 4 had almost identical infrared spectra with fraction 2 very similar to 3 and 4. The broad boiling ranges indicated mixtures.



(2) Benzene-1,4-bis-  
(methylphosphinic acid) (1388-38)

Experiment 1. A 1.1 g. portion of crude p-bis(dimethylaminomethylphosphino)benzene (fraction 3, vide supra) was dissolved by heating in 20 ml. of 6N hydrochloric acid. To this solution was added 3 ml. of 30% hydrogen peroxide and the mixture was evaporated to give a thick syrup which gradually solidified as a white crystalline solid. This solid was dissolved in 50 ml. of ethanol, concentrated to 20 ml. and 10 ml. of benzene was added. On cooling 0.390 g. of a white crystalline solid, m.p. 230-235°C., was obtained. Further concentration of the mother liquor yielded impure dimethylamine hydrochloride. After four recrystallizations of the crude solid from ethanol the product still had a wide melting range, 231-236°C. The sample was dried for 3 hrs. at 200°C. and analyzed. Anal. calcd. for  $C_8H_{12}P_2O_4$ : C, 41.04; H, 5.14; neut. eq. 117.1. Found: C, 41.18; H, 5.44; neut. eq., 118.8. The difunctional acid gave a single break in the pH curve. The pH at half-neutralization was 2.67 (0.149 g. in 100 ml. of water). The infrared spectrum of this material (Nujol mull) had the same broad P-OH bands at 3.75, 4.65, and 6.0  $\mu$  that are present in the diphenylphosphinic acid spectrum.

Experiment 2. The remaining 8.8 g. of crude p-bis-(dimethylaminomethylphosphino)benzene (fractions 3 and 4) was refluxed in 50 ml. of water. Dimethylamine was gradually evolved and after 2 hrs. the system became homogeneous at which time 5.0 ml. of 30% hydrogen peroxide was added. The mixture was evaporated to dryness on a steam bath yielding 8.1 g. of a light-yellow gummy solid. Two recrystallizations of this solid from ethanol yielded 2.54 g. of white crystalline solid, m.p. 228-230°C. The residue obtained from the mother liquor was gummy and reduced iodic acid. This material was treated with a slight excess of iodic acid and again evaporated to dryness. The residue was recrystallized from ethanol to yield an additional 2.2 g. of benzene-1,4-bis(methylphosphine acid), m.p. 228-230°C., raising the total yield to 4.74 g.

Both fractions 2 and 5 from the p-bis(dimethylamino-methylphosphino)benzene preparation were hydrolyzed and oxidized separately with hydrogen peroxide. Fraction 2 gave only a thick syrup which could not be crystallized. Fraction 5 gave 0.95 g. of a white crystalline solid, m.p. 170-178°C., which after recrystallization from 5 ml. of benzene followed by sublimation under high vacuum at 200-220°C. yielded long needles, m.p. 179-180°C. Anal. C, 43.37; H, 3.12. No further characterization was attempted.

(3) p-Bis(methylphosphino)benzene (1388-73)

A 2.544 g. (10.87 mmoles) sample of 1,4-benzene-bis-(methylphosphinic acid) was refluxed for 4 hrs. in 60 ml. of thionyl chloride to yield a clear solution. Evaporation of the solution in a stream of nitrogen left a solid residue which was insoluble in ether but was added as a slurry to a solution of 2 g. (57.2 mmoles) of lithium aluminum hydride in 150 ml. of refluxing ether. The stirred reaction mixture was maintained at reflux for 3 hrs. then hydrolyzed with 200 ml. of water, and the ethereal layer was separated and evaporated under nitrogen. No liquid residue was obtained.



## 5. Miscellaneous Intermediates

### a. Preparation of Neopentyl Chloride<sup>37</sup> (1157-21)

To 474.4 g. (6.575 moles) of neopentane in a 2 l. Pyrex glass vessel and illuminated with a 1000 watt tungsten lamp was added slowly with stirring 477.7 g. (6.736 moles) of chlorine. Two condensers in series, the first maintained at  $-20^{\circ}\text{C}$ . and the second at  $-78^{\circ}\text{C}$ ., were used to prevent the loss of reagents but permit escape of the hydrogen chloride. The temperature of the reaction mixture was held near  $-10^{\circ}\text{C}$ . (ice-salt bath) where a more rapid rate of addition of chlorine could be maintained. At higher temperatures (approximately  $10^{\circ}\text{C}$ .) a black tacky material developed in the solution. After addition of the chlorine the reaction mixture was warmed to room temperature and the volatile gases passed through two traps maintained at  $-78^{\circ}\text{C}$ . leading to a third trap at  $-196^{\circ}\text{C}$ . Neopentyl chloride and unreacted neopentane condensed at  $-78^{\circ}\text{C}$ . whereas the by-product hydrogen chloride passed through and was condensed at  $-196^{\circ}\text{C}$ . A small amount (1.8 g., 0.025 mole) of neopentane was recovered from the  $-196^{\circ}\text{C}$ . cooled trap on warming to  $-78^{\circ}\text{C}$ . to remove the hydrogen chloride. The neopentyl chloride-neopentane mixture was shaken with water to remove any dissolved hydrogen chloride and dried over anhydrous sodium sulfate followed by calcium sulfate. Distillation of the crude product on a 60 cm. spinning band column gave 215.8 g. (2.024 moles, 30.8%) of neopentyl chloride, b.p.  $81.5-82^{\circ}\text{C}/714-718\text{ mm.}$ , assaying 99.8% by vapor phase chromatography. A 10.4 g. (0.096 mole, assay 98.2%) forerun, b.p.  $80.5-81.5 (714-716\text{ mm.})$ , was recovered separately to provide a total of 226.2 g. (2.120 moles, 32.3% yield) of neopentyl chloride. A 56.6 g. quantity of neopentane was recovered from the distillation trap maintained at  $-196^{\circ}\text{C}$ .

### b. Preparation of 1-Chloro-2-(benzyloxy)ethane (1391-138)

Three drops of dry pyridine were added to 150 ml. of dry benzene and 23.2 ml. (0.323 mole) of thionyl chloride in a 500 ml. 4-neck, round bottom flask equipped with a 100 ml. addition funnel, stirrer, thermometer, and a water condenser vented through a drying tube. The reaction mixture was cooled to  $0^{\circ}\text{C}$ . and 50.0 ml. (0.3076 mole) of 2-(benzyloxy)ethanol was added from the addition funnel during 5 min. and the mixture was heated to reflux for 4 hrs. About 100 ml. of distilled water was added to the flask and the benzene phase was isolated, dried over sodium sulfate, and filtered. The benzene was distilled from the mixture at atmospheric pressure and the product was fractionated through a spinning band column at 48-50 mm. to give 49.36 g. (0.2893 mole, 92.4%, assay 98.6% by vapor phase chromatography) of 1-chloro-2-(benzyloxy)ethane  $n_D^{25} 1.5197$  (Lit.<sup>24</sup> 1.5204).

### c. Attempt to Prepare $\alpha$ -Bromo-methyl Benzyl Ether and $\beta$ -Bromoethyl Benzyl Ether (1391-86,89,100,103)

In a pair of parallel experiments, 43.9 ml. (0.63 mole) of methylene bromide (or 54.5 ml., 0.63 mole, of ethylene bromide) and 160 ml. of benzene were placed in a 500 ml. Morton flask equipped with a stirrer,



thermometer, 100 ml. addition funnel, and a water condenser. A mixture of 40.3 ml. (0.50 mole) of pyridine and 51.5 ml. (0.50 mole) of benzyl alcohol was added to each of the refluxing benzene solutions during 1 hr. After an additional 6 hrs. refluxing the cooled reaction slurries were filtered through sintered glass funnels. The filter cakes, 15.1 g. and 33.8 g., respectively, (presumably pyridinium bromide: calcd. Br, 49.9: found Br, 46.9, 43.1) were washed several times with 20 ml. portions of benzene. The combined washings and filtrates were dried over sodium sulfate, filtered, and the solvent was removed on a rotary film evaporator. Infrared and vapor phase chromatographic analyses of the resulting materials showed only starting materials to be present and, accordingly, the mixtures were not worked up further.

In a second pair of parallel experiments following the method of Marvel and Tanenbaum<sup>39</sup>, 51.5 ml. (0.50 mole) of benzyl alcohol, 160 ml. of distilled water, and 43.9 (0.63 mole) of methylene bromide (or 54.5 ml. 0.63 mole, of ethylene bromide) were placed in the same apparatus described above. A 24.6 g. (0.60 mole) quantity of sodium hydroxide was added as an aqueous solution during 1 hr. to each of the refluxing mixtures. The reaction mixtures were refluxed for an additional 20 hrs. (14 hrs. for the higher homolog), cooled to room temperature, and the two-phase reaction mixtures were transferred to 1000 ml. separatory funnels. Each aqueous phase was washed 3 times with 50 ml. portions of chloroform (benzene for the higher homolog). Each of the combined filtrates and washings were dried over sodium sulfate, filtered, and solvent was removed on a rotary film evaporator. Infrared and vapor phase chromatographic analyses of the resulting materials again indicated only the presence of starting materials.

d. Preparation of Low Molecular Weight Polyvinyl Chloride (1157-6,5,2,18,20)

Experiment 1. To 0.0981 g. (0.405 mmole) of benzoyl peroxide and 32.6 g. (384 mmoles) of methylene chloride in a 50 ml. bomb tube was added 1.4623 g. (23.40 mmoles) of vinyl chloride. After heating for 24 hrs. at 87-100°C. the tube was opened on the vacuum line and the volatile material was passed through a series of three -78°C. traps in which methylene chloride condensed and a -196°C. trap in which the vinyl chloride condensed. In this manner separation of the mixture was effected and provided 32.4 g. methylene chloride (v.t. 499 mm. at 26.5°C.) and 43.9 cc. (0.123 g., 1.96 mmoles, 8.4% recovery) of vinyl chloride. The solid product was dissolved in approximately 60 ml. of acetone and the extract was allowed to evaporate to dryness at room temperature. The resulting residue was dissolved in 6 ml. of tetrahydrofuran. The addition of 10 ml. of methanol caused the precipitation of a white solid which was separated by filtration. On addition of another 2 ml. of methanol to the filtrate, more of the white precipitate formed and was removed by filtration. The filtrate was concentrated to give a yellow liquid containing a white solid. This residue was dissolved in 4 ml. of tetrahydrofuran to which was added 12 ml. of methanol. On concentration, the white precipitates that formed were removed by filtration and decantation. After the solvent was completely removed, 0.4556 g. (31%) of a yellow viscous material remained, the molecular weight of which was 555 (Neumayer) corresponding to a D.P. of 7.5.



In a preliminary experiment, an evacuated 5 ml. bomb tube containing 0.0725 g. (0.299 mmole) of benzoyl peroxide, 10.6644 g. (125.55 mmole) of methylene chloride and 2.5803 g. (41.28 mmole) of vinyl chloride was heated for 24 hrs. at 78-84°C. The volatile material was fractionated, as described above, and found to consist of 0.0421 g. (0.67 mmole, 1.6% recovery) of vinyl chloride and 10.1 g. of methylene chloride (v.t., 430 mm. at 24°C.). The solid residue was extracted with approximately 15 ml. of acetone to which was added approximately 5 ml. of methanol. A hard, yellow precipitate formed, which was believed to be a benzoyl peroxide decomposition product seemingly similar to that described by other workers<sup>40</sup>. On further addition of methanol (approximately 35 ml.), 1.6917 g. of white polyvinyl chloride formed having a molecular weight (Neumayer) of 4646 corresponding to a D.P. of 73.

Experiment 2. In a 5 ml. heavy-wall Pyrex tube was condensed 0.361 g. (5.78 mmole) of vinyl chloride in vacuo and the tube was sealed. After 142 min. of exposure to ultraviolet radiation (Fluorolight ultraviolet lamp) the tube was opened and the volatile material, 0.326 g. (5.22 mmole, 90.6% recovery) of vinyl chloride (v.t., 18.0 mm. at -78°C.), was removed. No liquid or solid polymerization products were observed in the reaction tube.

Experiment 3. The recovered vinyl chloride from Experiment 2 (0.326 g., 5.22 mmole) was condensed in another tube of similar type, sealed under vacuum and heated at 75°C. for 15 hrs. and at 100°C. for 116 hrs. On opening the tube under vacuum, 0.186 g. (2.98 mmole, 57.1% of vinyl chloride was recovered. The low recovery of vinyl chloride was the result of mechanical losses since no polymerization products were observed.

Experiment 4. In an exploratory experiment conducted on a qualitative basis, approximately 2-3 g. of polyvinyl chloride telomer, obtained from Escambia Chemical Corporation, was dissolved in 20 ml. of tetrahydrofuran. To this transparent solution was added 20 ml. of methanol which effected the precipitation of a white solid. After removal of the solid, the filtrate was evaporated to dryness at aspirator pressure to yield a viscous, yellow liquid which had a molecular weight of 472 (Neumayer) corresponding to a D.P. of 5.1 (assuming carbon tetrachloride was used as the chain transfer agent).

In a quantitative second experiment, 4.0372 g. of polyvinyl chloride telomer, obtained from Escambia Chemical Corporation, was dissolved in 16 ml. of tetrahydrofuran. The high molecular weight polymer was precipitated on the addition of 20 ml. of methanol and removed. The filtrate, on evaporation, gave 1.8959 g. (47%) of a viscous, yellow liquid which had a molecular weight of 458 (Neumayer) corresponding to a D.P. of 4.8 (assuming carbon tetrachloride was used as the chain transfer agent).

e. Preparation of Methylphenyl-  
phosphinic Acid (W-1805-33)

A solution of 5.7 g. (32.2 mmole) of iodic acid in 80 ml. of water was added dropwise to a magnetically stirred mixture of methylphenylphosphine (5.0 g., 36.9 mmole, 91.5% by VPC) and 40 ml. water in an ice-water cooled flask vented through a mercury bubbler. The water solution was then



boiled until colorless to remove by-product iodine. Hydriodic acid was added to the clear solution to convert excess iodic acid to iodine which was removed as before. The solution was concentrated and on cooling deposited needles of methylphenylphosphinic acid which after two recrystallizations from absolute ethanol provided 4.2 g. (26.9 mmoles, 73% yield) of colorless needles, m.p. 134-136°C. Anal. calcd. for  $C_7H_9PO_2$ : C, 53.85; H, 5.81; neut. eq. and M.W., 156.12. Found: C, 53.82; H, 5.71; neut. eq., 155.0; M.W. 398 (Neumayer in benzene), 354 (microbulliometric in benzene).

A curve obtained on titration of 0.2353 g. (1.507 meq.) of methylphenylphosphinic acid dissolved in 100 ml. of water with 0.1072N NaOH gave a  $pK_a$  at half neutralization of 2.96.



#### IV. NEW APPROACHES TO THERMALLY STABLE POLYMERS

##### A. Discussion

A survey of new approaches to thermally stable polymer systems based on P-N, Si-O-C<sup>O</sup>, and B-N bonding systems has been continued.

##### 1. Phosphorus-Nitrogen Chemistry

##### a. Nomenclature of Phosphorus Compounds

A simplified nomenclature has been used for the organophosphorus compounds in this work. The principles used in selecting the nomenclature are: (1) trivial names for common materials such as trimethyl phosphite, triphenyl phosphate, triphenylphosphine oxide, etc., have been retained; (2) trivalent phosphorus compounds are named as phosphines; (3) "pentavalent" phosphorus compounds are named either as -phospon- or phosphorane. Illustrative examples are given in Table XIV. Other nomenclature systems have been summarized by Van Wazer<sup>41</sup>.

##### b. Introduction

We have previously reported<sup>42</sup> the preparation of diphenylphosphonyl azide (IIIa) from diphenylphosphonyl chloride and sodium azide (Equation 44). The unexpected thermal stability of diphenylphosphonyl azide (in contrast to the facile thermal rearrangement of carboxylic azides in the Curtius Reaction), and its reaction with triphenylphosphine (Equation 48) to give diphenylphosphonimidotriphenylphosphorane (IVa) prompted a further study of this new approach to P-N=P bonding systems.

##### c. Intermediates

The diarylphosphonic acids (I a-c) required as starting materials were synthesized by the reaction of the appropriate Grignard reagent with either phosphorus oxychloride or N,N-diethylaminophosphonyl dichloride (Equation 41) in yields of 20-50%.



TABLE XIV

Illustrative Examples of  
Nomenclature for Phosphorus Compounds

Formula	Name
$\text{C}_6\text{H}_5\text{PCl}_2$	phenyldichlorophosphine
$(\text{C}_6\text{H}_5)_2\text{PCl}$	diphenylchlorophosphine
$(\text{C}_6\text{H}_5)_3\text{P}$	triphenylphosphine
$\text{C}_6\text{H}_5\text{P}(\text{CH}_3)_2$	phenyldimethylphosphine
$[(\text{CH}_3)_2\text{N}]_3\text{P}$	tris-(dimethylamino)phosphine
$(\text{C}_6\text{H}_5\text{O})_3\text{P}=\text{O}$	triphenyl phosphate
$\begin{array}{c} \text{O} \\ \uparrow \\ (\text{C}_6\text{H}_5\text{O})_2\text{PCl} \end{array}$	diphenoxyphosphonyl chloride
$\begin{array}{c} \text{O} \\ \uparrow \\ \text{C}_6\text{H}_5\text{P}(\text{OH})_2 \end{array}$	phenylphosphonic acid
$\begin{array}{c} \text{O} \\ \uparrow \\ \text{C}_6\text{H}_5\text{PCl}_2 \end{array}$	phenylphosphonyl dichloride
$\begin{array}{c} \text{O} \\ \uparrow \\ (\text{C}_6\text{H}_5)_2\text{POH} \end{array}$	diphenylphosphonic acid
$\begin{array}{c} \text{O} \\ \uparrow \\ (\text{C}_6\text{H}_5)_2\text{PCl} \end{array}$	diphenylphosphonyl chloride
$\begin{array}{c} \text{S} \\ \uparrow \\ (\text{C}_6\text{H}_5)_2\text{PCl} \end{array}$	diphenylthiophosphonyl chloride
$\begin{array}{c} \text{O} \\ \uparrow \\ (\text{C}_6\text{H}_5)_2\text{PN}_3 \end{array}$	diphenylphosphonyl azide
$\begin{array}{c} \text{S} \\ \uparrow \\ (\text{C}_6\text{H}_5)_2\text{PN}_3 \end{array}$	diphenylthiophosphonyl azide

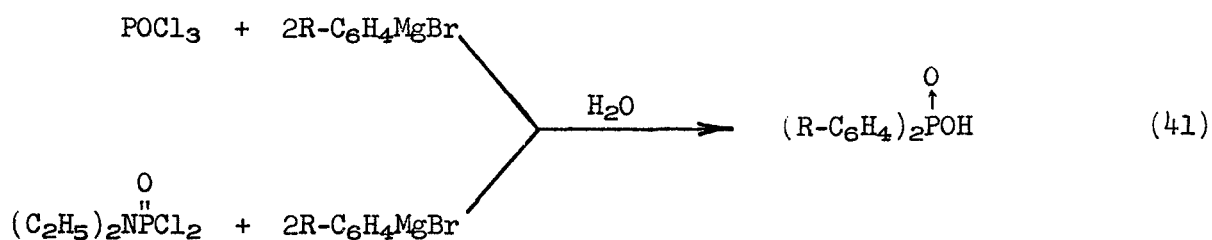


TABLE XIV (CONT.)

Illustrative Examples of  
Nomenclature for Phosphorus Compounds

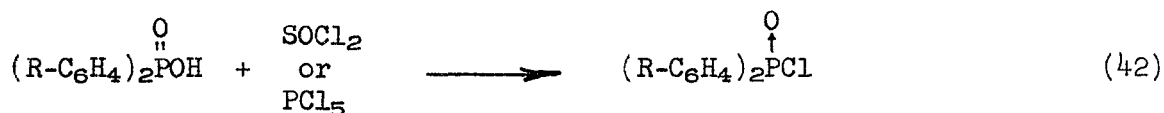
Formula	Name
$\begin{array}{c} \text{O} \\ \uparrow \\ (\text{C}_6\text{H}_5)_2\text{POCH}(\text{CH}_3)_2 \end{array}$	isopropyl diphenylphosphonate
$\begin{array}{c} \text{O} \\ \uparrow \\ (\text{C}_6\text{H}_5)_2\text{PNHC}_6\text{H}_5 \end{array}$	diphenylphosponanilide
$\begin{array}{c} \text{O} \\ \uparrow \\ (\text{C}_6\text{H}_5)_2\text{PN}=\text{P}(\text{C}_6\text{H}_5)_3 \end{array}$	diphenylphosphonimidotriphenylphosphorane
$\begin{array}{c} \text{O} \quad \text{CH}_3 \\ \uparrow \quad   \\ (\text{C}_6\text{H}_5)_2\text{PN}=\text{PC}_6\text{H}_5 \\   \\ \text{CH}_3 \end{array}$	diphenylphosphonimidophenyldimethylphosphorane





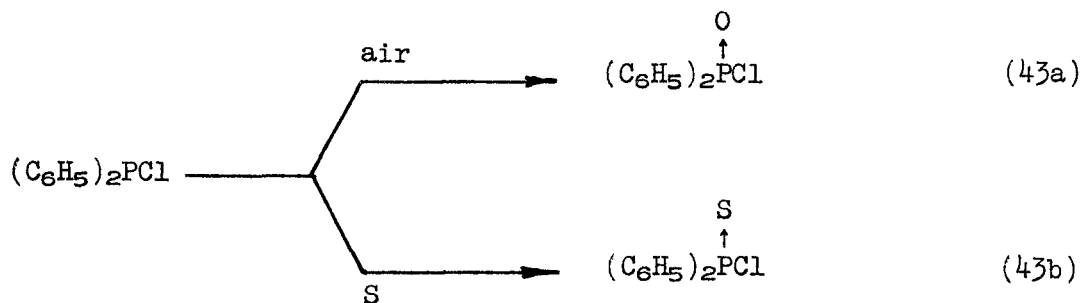
- Ia R = H  
 b R = p-CH<sub>3</sub>  
 c R = p-Cl

The diarylphosphonic acids were converted to the corresponding diarylphosphonyl chlorides (II a-c) by reaction with thionyl chloride or phosphorus pentachloride (Equation 42). Diphenylphosphonyl chloride (IIa) was prepared by air-oxidation of



- IIa R = H  
 b R = p-CH<sub>3</sub>  
 c R = p-Cl

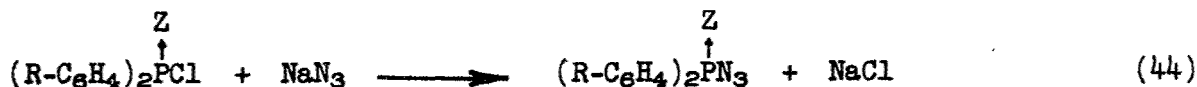
diphenylchlorophosphine (Equation 43a) and diphenylthiophosphonyl chloride was prepared in quantitative yield by sulfur oxidation of diphenylchlorophosphine at reflux in benzene (Equation 43b).





#### d. Diarylphosphonyl Azides

The diarylphosphonyl chlorides (II) were converted to the corresponding diarylphosphonyl azides (III a-d) by allowing approximately equal molar quantities of phosphonyl chloride and sodium azide to react in anhydrous pyridine (Equation 44).

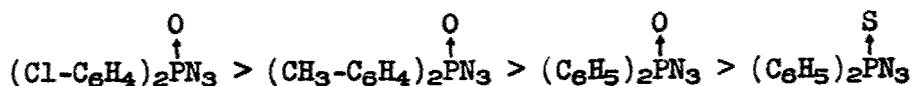


- IIIa R = H, Z=O  
 b R = p-CH<sub>3</sub>, Z=O  
 c R = p-Cl, Z=O  
 d R = H, Z=S

Diphenyl-(IIIa), bis-(p-tolyl)- (IIIb), bis-(p-chlorophenyl)- (IIIc), and diphenylthiophosphonyl azides (IIId) were prepared and characterized. It was previously reported that pyridine, acetonitrile, and benzene were suitable solvents for the preparation of diarylphosphonyl azides. A reinvestigation of the reaction in benzene indicates that this is not a suitable solvent under the same conditions that give essentially quantitative yields of azide when pyridine is used.

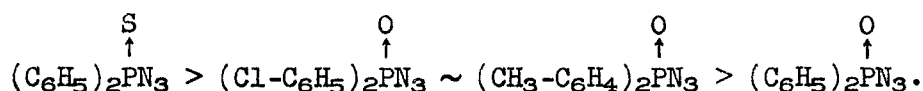
#### e. Properties of Diarylphosphonyl Azides

Diarylphosphonyl azides, as a class of azides, appear to have unusual thermal stability. Diphenylphosphonyl azide was distilled at 137-140°C. at 0.05 mm.; bis-(p-tolyl)-phosphonyl azide distilled at 190-195°C. at 0.5 mm. with slow decomposition; bis-(p-chlorophenyl)phosphonyl azide distilled at 10<sup>-5</sup> mm. without apparent decomposition; diphenylthiophosphonyl azide turned red and could be distilled only with difficulty at 10<sup>-4</sup> mm. The infrared spectra of crude (yellow) and distilled diphenylthiophosphonyl azide (red) were identical. The red color changed to yellow on standing; there was no apparent evolution of nitrogen accompanying the color changes from yellow-to-red and red-to-yellow. These observations suggest the following qualitative order of thermal stability for the diarylphosphonyl azides:



The hydrolytic stability of the diarylphosphonyl azides varies markedly; diphenylphosphonyl azide appears to hydrolyze in a matter of minutes, whereas, under the same conditions diphenylthiophosphonyl azide is not completely hydrolyzed after several hours. Qualitatively, the relative order of hydrolytic stability appears to be

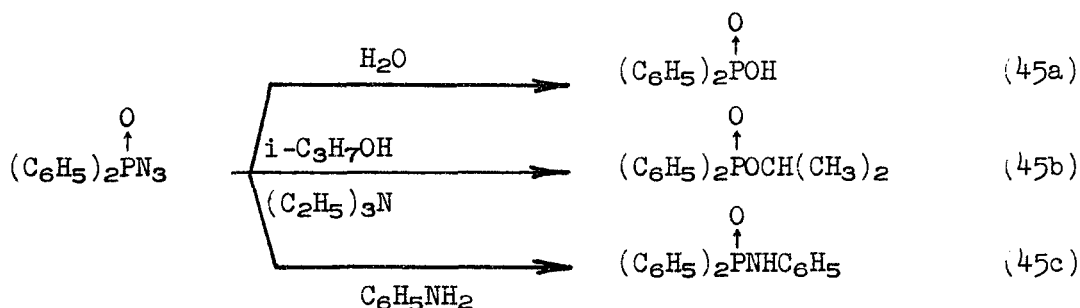




It also appears that diphenylphosphonyl azide has excellent storage stability; a sample which had been purified by distillation exhibited no decomposition on storage for 8 months. Also, a sample of crude material exhibited no decomposition in the presence of 316 stainless steel during several weeks.

#### f. Reactions of Diarylphosphonyl Azides

Diphenylphosphonyl azide undergoes solvolytic reactions such as hydrolysis (Equation 45a), alcoholysis (Equation 45b), and aminolysis (Equation 45c).



The alcoholysis reaction (Equation 45b) must be performed under anhydrous conditions to prevent the preferential formation of diphenylphosphonic acid. Furthermore, the alcoholysis reaction did not occur readily except in the presence of a tertiary amine. The reactions of diphenylphosphonyl azide are summarized in Figure 3.

Arenesulfonyl azides have been reported to undergo reaction with aromatic compounds to yield arenesulfonanilides<sup>43</sup>. It appeared possible that a similar reaction between diarylphosphonyl azides and aromatic compounds might occur. Such a reaction would extend the chemistry of the phosphonyl azides and would provide a convenient route to a variety of phosphonanilides (Equation 46).





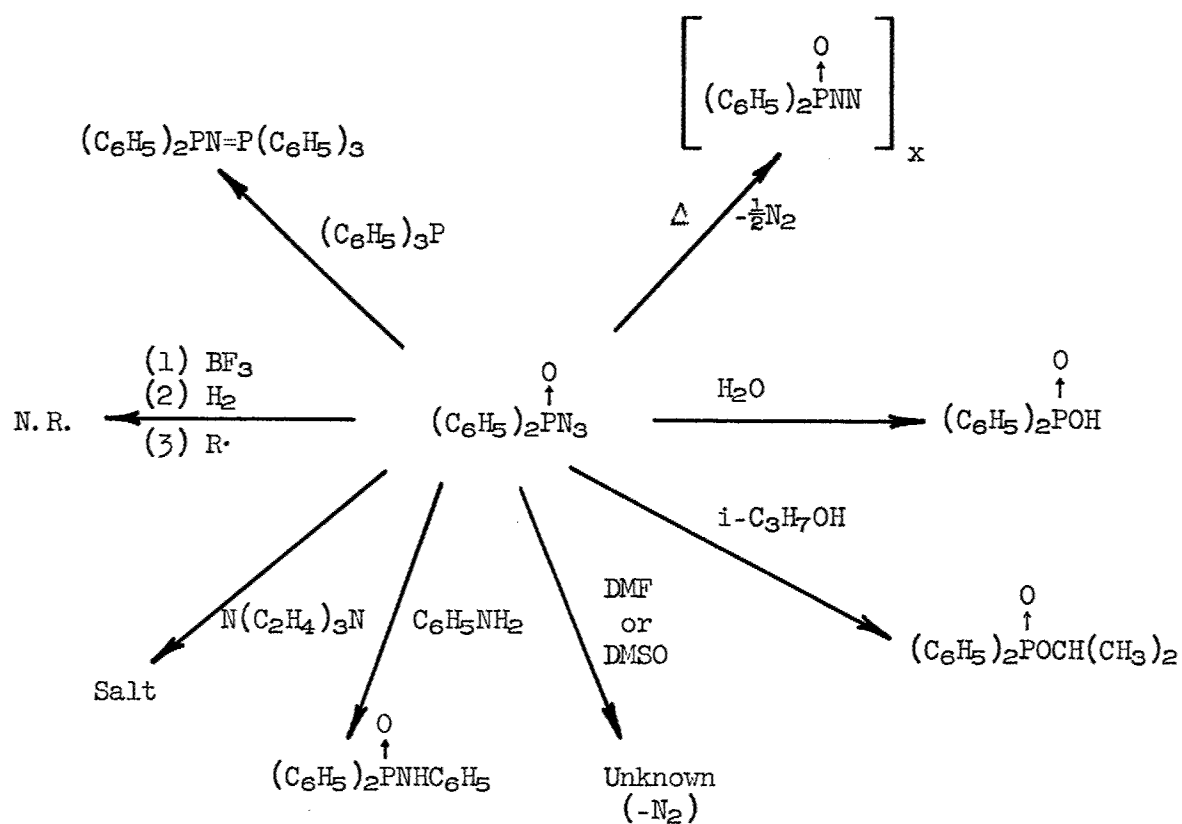
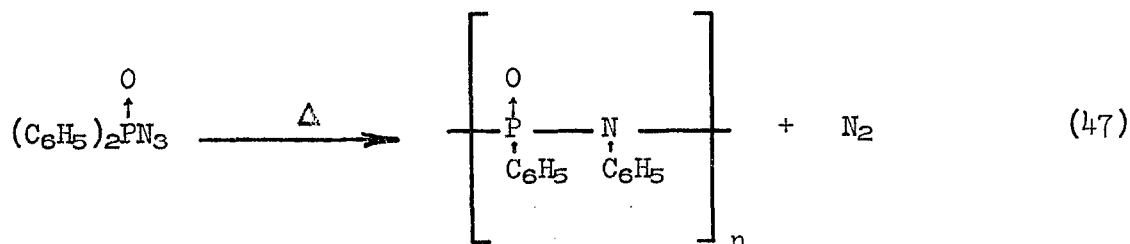


Figure 3. Reactions of Diphenylphosphonyl Azide



Such reactions were attempted in refluxing benzene and in p-xylene using azo-bis-isobutyronitrile as a radical source. In both cases, no phosphonanilide was obtained and no nitrogen evolution was observed; infrared examination of the residual liquids indicated that the strong azide absorption at  $4.65\mu$  was unchanged. In this connection, pyridine appears to be an excellent solvent for the preparation of diarylphosphonyl azides with no apparent reaction occurring with the solvent. However, arenesulfonyl azides have been shown to react with pyridine<sup>44,45</sup>.

It was previously shown<sup>42</sup> that diphenylphosphonyl azide underwent thermolysis at 220-250°C. to yield one-half of the nitrogen based on Equation 47.



In a further attempt to cause the rearrangement shown in Equation 47 using boron trifluoride in ether at reflux for 48 hrs., there was no nitrogen evolution or other evidence of reaction; infrared examination of the reaction mixture indicated that little or no reaction had occurred.

It was previously observed<sup>42</sup> that diphenylphosphonyl chloride reacted with sodium azide in dimethylformamide to give an immediate evolution of nitrogen. However, when diphenylphosphonyl azide was added to dimethylformamide (dried over anhydrous sodium sulfate), no nitrogen evolution was observed. When the dimethylformamide was dried by distillation from calcium hydride it was found to contain some free amine, and the impure dimethylformamide appeared to cause an unexplained large gas evolution (vide infra). It has also been found that diphenylphosphonyl azide reacts with dimethylsulfoxide with the liberation of nitrogen. The nature of the products obtained in the dimethylformamide and dimethylsulfoxide reactions has not been determined.

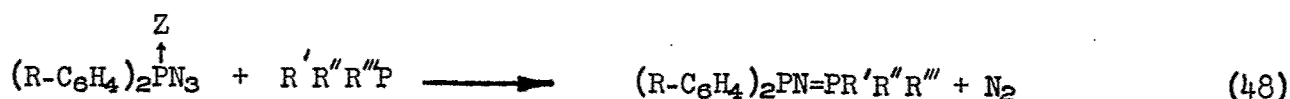
Diarylphosphonyl azides react with trivalent phosphorus compounds to yield phosphoranes. This reaction is discussed in Section g.

#### g. Phosphoranes

##### (1) From Phosphonyl Azides

Diarylphosphonyl azides react with trivalent phosphorus compounds (Equation 48) to provide diarylphosphonimidophosphoranes (IV a-g).





- IVa  $R=H$ ;  $R'R''R'''=C_6H_5$ ;  $Z=O$   
 b  $R=p-Cl$ ;  $R'R''R'''=C_6H_5$ ;  $Z=O$   
 c  $R=p-CH_3$ ;  $R'R''R'''=C_6H_5$ ;  $Z=O$   
 d  $R=H$ ;  $R'R''R'''=C_6H_5$ ;  $Z=S$   
 e  $R=H$ ;  $R'R''R'''=p-Cl-C_6H_4$ ;  $Z=O$   
 f  $R=H$ ;  $R'R''R'''=p-CH_3-C_6H_4$ ;  $Z=O$   
 g  $R=H$ ;  $R'R''=CH_3$ ;  $R'''=C_6H_5$ ;  $Z=O$

Diphenylphosphonyl azide reacts slowly with triphenylphosphine in ether to yield diphenylphosphonimidotriphenylphosphorane with the concurrent liberation of equal molar quantities of nitrogen. However, pyridine appears to be a more generally useful solvent for this reaction. Whereas diphenylphosphonyl azide reacts only slowly in ether at reflux, the reaction is essentially quantitative in pyridine at reflux within about one-tenth the time required in ether.

It was previously observed<sup>46</sup> that the liberation of nitrogen from the reaction of phenyldimethylphosphine with diphenylphosphonyl azide in ether at room temperature was so vigorous that it could not be simply controlled. It has now been found that diphenylphosphonyl azide and phenyldimethylphosphine react in pyridine solution at 0°C. to give a vigorous but controllable evolution of nitrogen and a good yield of diphenylphosphonimidophenyldimethylphosphorane (IVg).

In a survey of the scope of phosphorane formation, diphenylphosphonyl azide was allowed to react with a variety of Lewis bases in different solvents (Table XV). Qualitatively, it appears that the rate of reaction of the various Lewis bases with diphenylphosphonyl azide is in the order,

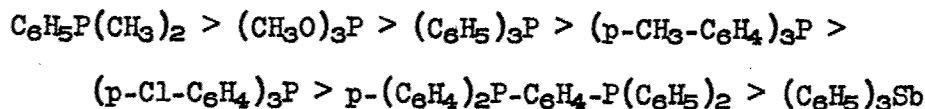




TABLE XV

Reaction of Diphenylphosphonyl Azide  
with Various Lewis Bases in Various Solvents

Expt. No.	Base	All Reactants, Moles	Nitrogen, cc.		Reaction Time, Hrs.	Remarks
			Theory	Found		
1323-186	$\text{C}_6\text{H}_5\text{P}(\text{CH}_3)_2$	0.065	1456	Lost	-	Extremely exothermic evolution of gas in cold ether.
1134-111	$\text{C}_6\text{H}_5\text{P}(\text{CH}_3)_2$	0.015	340	300	0.5	Pyridine at 0° C.
1134-67	$(\text{CH}_3\text{O})\text{P}$	0.01	224	230	0.5	Rapid evolution of nitrogen in refluxing pyridine: black residue.
1134-43	$(\text{C}_6\text{H}_5)_3\text{Sb}$	0.0088	197	120	18	In refluxing diglyme.
1134-32	$(\text{p-CH}_3\text{C}_6\text{H}_4)_3\text{P}$	0.013	291	254	6	Infrared similar to other phosphoranes; in ether solvent.
1134-79	$(\text{p-ClC}_6\text{H}_5)_3\text{P}$	0.015	332	350	0.75	Product M.W. 585; Theory, 581; pyridine solvent.
1323-189	$(\text{C}_6\text{H}_5)_2\text{PC}_6\text{H}_4\text{P}(\text{C}_6\text{H}_5)_2$	0.01*	224	220	6	In tetrahydrofuran solvent.

\* The biphosphine used was 0.005 mole.

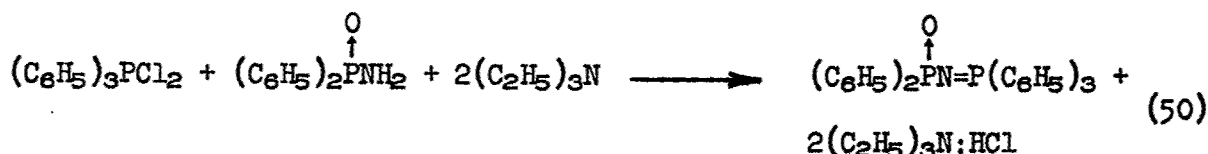


## (2) Attempted Preparation from Diphenylphosphonamide

Since it has been reported that triphenyldichlorophosphorane reacts with aniline to yield phenyliminotriphenylphosphorane<sup>47</sup> (Equation 49), it was anticipated that a similar reaction between diphenylphosphonamide and triphenyldichlorophosphorane would offer an alternate route

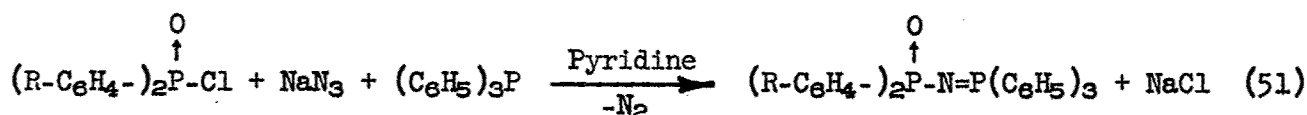


to diphenylphosphonimidotriphenylphosphorane (Equation 50). However, none of the desired diphenylphosphonimidotriphenylphosphorane was obtained from the one experiment performed.



## (3) In Situ Procedure

An in situ procedure for the preparation of diarylphosphonimidotriphenylphosphorane (IV) and other metalloid phosphoranes has been developed which does not require isolation of the phosphonyl azide or other metalloid azide. In the in situ procedure, a mixture of sodium azide and triphenylphosphine in pyridine solvent is warmed to a gentle reflux under an argon atmosphere and then the phosphonyl chloride in pyridine is slowly added at such a rate that an easily controlled evolution of nitrogen is obtained (Equation 51). The pyridine is removed at reduced pressure and the solid residue



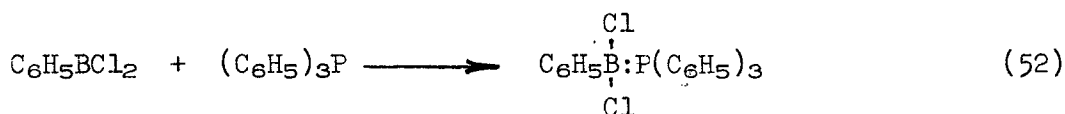
washed with ether and ammonium hydroxide. The in situ procedure offers some advantages in choice of solvent. For example, when diphenylphosphonyl chloride and sodium azide are allowed to react in dimethylformamide there is an immediate evolution of nitrogen indicating decomposition of the azide<sup>42</sup> (vide supra). However, when the diphenylphosphonyl chloride was added to a hot solution of sodium azide and triphenylphosphine in dimethylformamide a good yield of diphenylphosphonimidotriphenylphosphorane was obtained.

A useful modification of the in situ procedure just described involves the addition of the phosphonyl chloride to sodium azide in pyridine followed by removal of the precipitated sodium chloride by filtration. This leaves a pyridine solution of the phosphonyl azide which can then be allowed to react with a phosphine to yield a phosphorane. Using the in situ



procedure most of the phosphorane preparations can be completed within 10-15 minutes in a small run (10 g.) and the yields of phosphorane are generally about 95%.

The in situ procedure for the preparation of phosphoranes was also used to make a cursory survey of the generality of metalloid azide reaction with triphenylphosphine. The results are given in Table XVI. These preliminary results indicate that triphenylchlorostannane and phenyldichloroborane did not undergo reaction. However, the recent preparation of dimesitylazidoborane<sup>48</sup> from dimesitylfluoroborane suggests that phenylazidoboranes are capable of existence. One of the reasons that phenyldichloroborane failed to react in the in situ procedure for phosphorane formation may have been the result of complex formation between phenyldichloroborane with triphenylphosphine (Equation 52).



Lieber and Keane<sup>49</sup> have recently reported the preparation of triphenyllead azide. By analogy it might be expected that triphenylchlorostannane would form an azide and, indeed, azide formation might have occurred without liberation of nitrogen. For example, Leffler, et al.<sup>50</sup> found that triphenylmethyl azide formed a complex with triphenylphosphine which was stable in neutral solution.

#### h. Anomalous In Situ Reaction. Formation of Diphenylphosphinic Nitride

When an attempt was made to use the in situ procedure for the preparation of diphenylthiophosphonimidotriphenylphosphorane, none of the desired material was obtained. Instead, an 8% per cent yield of triphenylphosphine sulfide and a yellow, gummy material which was insoluble in benzene were obtained (Equation 53).

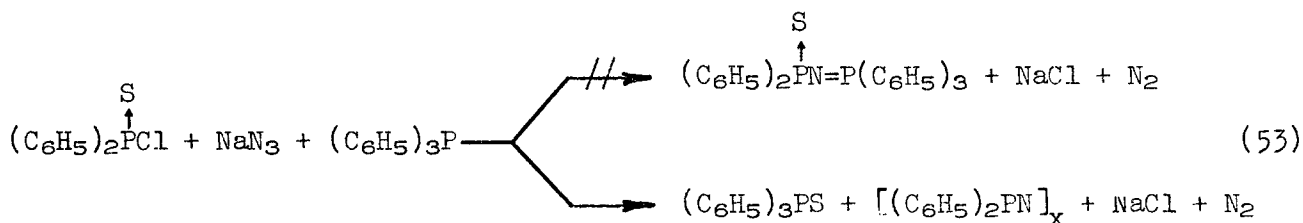




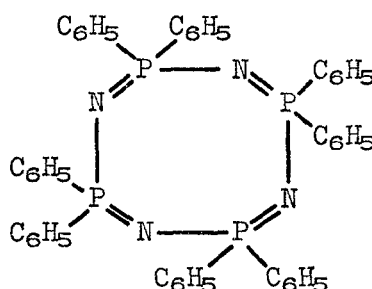
TABLE XVI

In Situ Procedure: Survey Reactions of Triphenylphosphine,  
Sodium Azide, and Groups III, IV, and V Chlorides

Expt. No.	Reactants, Moles		Nitrogen, cc.			Remarks	
	Halide	NaN <sub>3</sub> and (C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> P	Theory	Found	Reaction Time, Hrs.		
1134-63	(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SnCl	0.01	0.01	224	nil	64	Pyridine-toluene mixture at reflux.
1134-89	(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> SnCl	0.01	0.01	224	nil	24	Dimethylformamide at reflux.
1134-93	C <sub>6</sub> H <sub>5</sub> BCl <sub>2</sub>	0.019	0.038	851	nil	64	Toluene at reflux.
1134-66	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> PCl	0.01	0.01	224	nil	18	Pyridine at reflux.
1134-90		0.01	0.01	224	206	0.25	Dimethylformamide at reflux.
1134-64	(C <sub>6</sub> H <sub>5</sub> O) <sub>2</sub> POCl	0.01	0.01	224	146	5	First 110 cc. N <sub>2</sub> in 1 hr., residue a black gum; pyridine at reflux.
1134-65	(C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> PSCl	0.01	0.01	224	214	3.5	Black-brown residue partially soluble in water and in ether; pyridine at reflux.
1134-46	C <sub>6</sub> H <sub>5</sub> POCl <sub>2</sub>	0.012	0.025	544	450	24	Product M.W. 661; Theory 677; pyridine at reflux.
1134-74	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> SiCl <sub>2</sub>	0.005	0.01	224	224	2	Granular residue, reacts with water to give triphenylphosphine oxide; pyridine at reflux.
1134-82	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> SiCl <sub>2</sub>	0.005	0.01	224	224	24	Residue now unaffected by water. Infrared similar to other phosphoranes.
1134-92	p-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> Cl	0.01	0.01	224	246	25	Pyridine at reflux, no nitrogen evolved until triphenylphosphine added.
1134-76	POCl <sub>3</sub>	0.005	0.015	336	320	24	Brown, tacky residue, pyridine at reflux.

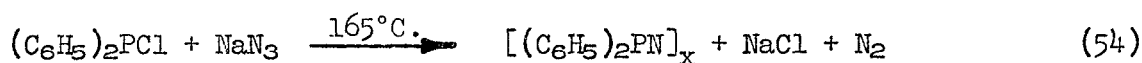


After heating a portion of the yellow material at 275-280°C. for 3 hrs. in a high vacuum, it was extracted with benzene. A white solid was obtained from the benzene extract which was identified as diphenylphosphinic nitride tetramer (V)\* by comparison of the melting point and infrared spectrum with those of an authentic sample.

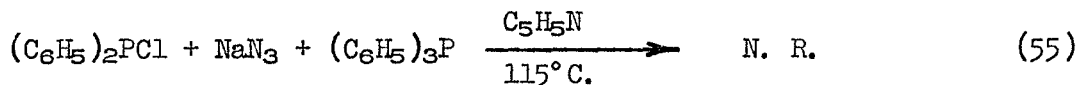


V

Herring<sup>51</sup> found that the reaction of diphenylchlorophosphine and sodium azide at 165°C. yielded a mixture of diphenylphosphinic nitride polymers (Equation 54).



However, when we attempted to prepare diphenylphosphinimidotriphenylphosphorane by the in situ reaction of diphenylchlorophosphine, sodium azide, and triphenylphosphine in pyridine at 115°C., there was no evidence of reaction (Equation 55).

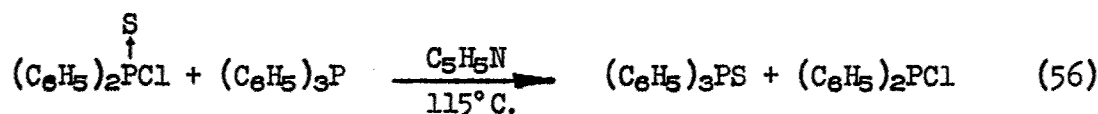


\* We wish to thank Mr. D. L. Herring, U. S. Naval Ordnance Laboratory, Corona, California, for a sample of diphenylphosphinic nitride tetramer and its infrared spectrum.

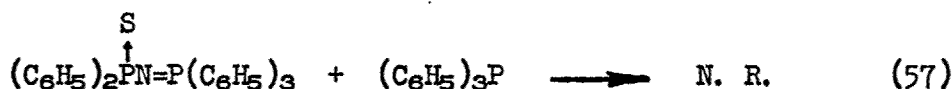


On the other hand, while the in situ reaction of diphenylthiophosphonyl chloride sodium azide, and triphenylphosphine underwent reaction in pyridine to yield a diphenylphosphinic nitride polymer mixture (Equation 53), diphenylthiophosphonyl azide reacted readily with triphenylphosphine in pyridine solution (Equation 48) to give an 87% yield of diphenylthiophosphonimidotriphenylphosphorane. In contrast, diphenylphosphonimidotriphenylphosphorane was obtained in 85% yield from diphenylphosphonyl azide (Equation 48) and in 97% yield by the in situ reaction of diphenylphosphonyl chloride, sodium azide and triphenylphosphine (Equation 51).

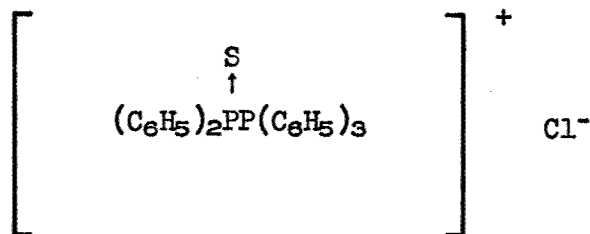
In an attempt to better understand this anomalous in situ reaction of diphenylthiophosphonyl chloride, sodium azide, and triphenylphosphine (Equation 53), it was found that diphenylthiophosphonyl chloride and triphenylphosphine react in pyridine at 115°C. to form triphenylphosphine sulfide in about 95% yield (Equation 56).



It seems unlikely, however, that Equation 56 represents the first step in the formation of diphenylphosphinic nitride polymer, since diphenylchlorophosphine was not observed to react under the same conditions (Equation 55). It was also determined that diphenylthiophosphonimidotriphenylphosphorane does not react with triphenylphosphine under the same conditions (Equation 57).



The above information and the facts that phosphonyl chlorides and diphenylphosphonyl azide form salts with amines (Fig. 3), suggest that the intermediate in the formation of triphenylphosphine sulfide and diphenylphosphinic nitride polymer might be a displacement, or a rearrangement reaction of a phosphonium salt, such as VI.



VI



### i. Properties of Phosphoranes

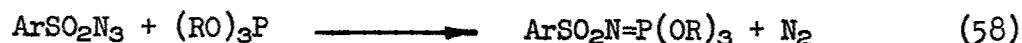
In preparing a large quantity of diphenylphosphonimidotriphenylphosphorane by the in situ procedure (Equation 51) the product obtained had a higher melting point (170-171°C.) than the product first obtained (149-150°C.)<sup>52</sup> by the reaction of diphenylphosphonyl azide with triphenylphosphine (Equation 48). Subsequent reactions of diphenylphosphonyl azide and triphenylphosphine gave the higher melting product. Elemental analyses and molecular weights were virtually the same for both products. Solution infrared and ultraviolet spectra of both materials were identical but shifts in several absorption bands were observed on comparison of the infrared spectra of the solids in potassium bromide pellets. A sample of the lower melting material which had been standing for several months had a wide melting range, 147-167°C., which suggests a slow conversion of low-melting to high-melting material. The low-melting material was readily converted to the high-melting material by recrystallization from isopropyl alcohol-water mixture. Although it is conceivable that the observed differences in physical properties are due to a difference in purity, the data suggest that diphenylphosphonimidotriphenylphosphorane exhibits two crystal forms or can exist in two geometric forms (*vide infra*).

When diphenylphosphonimidotriphenylphosphorane was heated in an evacuated tube at 216-244°C. for 20 hrs., a glass was obtained the infrared spectral absorptions of which were in between those of the high and low melting forms discussed above. However, recrystallization of the glass from isopropyl alcohol-water mixture, gave an essentially quantitative recovery of diphenylphosphonimidotriphenylphosphorane melting at 170-171°C.

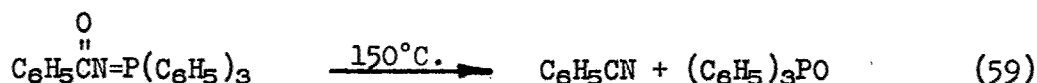
The general thermal and oxidative stability of the phosphoranes was demonstrated by dropping samples of the materials onto a heated copper block as previously described<sup>16</sup>. Diphenylphosphon-, bis-(p-chlorophenyl)-phosphon-, bis-(p-tolyl)phosphon-, and diphenylthiophosphonimidotriphenylphosphorane, and diphenylphosphonimidophenyldimethylphosphorane did not auto-ignite up to the temperature limit of the apparatus which was approximately 450°C. Furthermore, diphenylphosphonimidotriphenylphosphorane would not support combustion; it burned only when in direct contact with a Bunsen flame.

All of the phosphoranes isolated and characterized were found to be hydrolytically stable toward warm dilute ammonium hydroxide and dilute hydrochloric acid. In addition, the hydrolytic stability of diphenylphosphonimidotriphenylphosphorane was tested under more vigorous conditions. It was found to be stable toward 6N sulfuric acid at 100°C. for 18 hrs. and to be stable toward boiling alcoholic sodium hydroxide for 18 hrs. The combination of excellent hydrolytic, oxidative and thermal stabilities of the diarylphosphonimido-phosphoranes appear to be much better than the most closely related materials containing phosphorus-nitrogen bonds. For example, the preparation of a series of sulfonimidophosphoranes having relatively good thermal stability but having poor hydrolytic stability was reported recently (Equation 58).<sup>53</sup> Also, benzoimidotriphenylphosphorane has been reported to undergo rearrangement



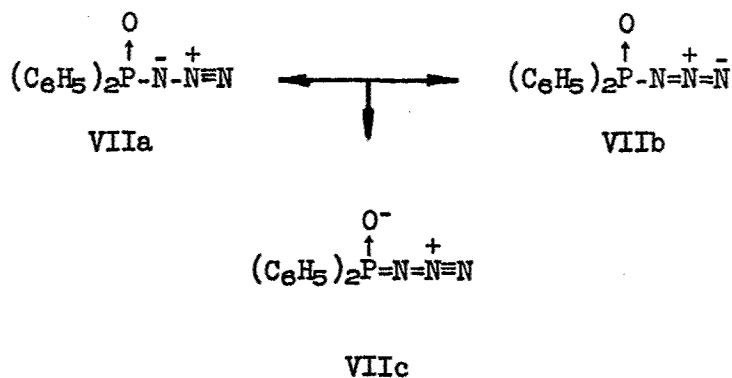


at 150°C. (Equation 59) and phenyliminotriphenylphosphorane is cleaved by hydrochloric acid (Equation 60).<sup>54</sup>



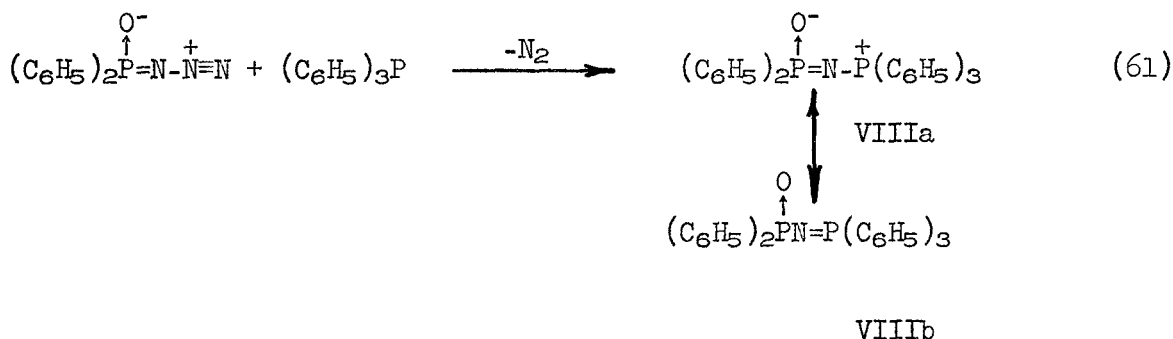
#### j. Structure and Spectra

The unusual properties of the diarylphosphonyl azides and diarylphosphonimidophosphoranes can be rationalized by considering the resonance forms which contribute to the total structure (VII a-c).



Infrared absorptions at 1265 cm<sup>-1</sup> (P=N) and at 1230 cm<sup>-1</sup> (P → O) suggest that the phosphonyl azides exist primarily as the charge-separated structure, VIIc. Structure VIIc is also suggested by the reaction of the azides with trivalent phosphorus compounds to yield phosphoranes (Equation 61).





There are insufficient data available to draw definite conclusions concerning the nature of the intermediate in the reaction of phosphonyl azides with trivalent phosphorus compounds. By analogy with the sulfonyl azides, it might be argued that a highly reactive triplet state nitrogen would obtain; however, this does not appear to be the case up to temperatures of about 137°C. as evidenced by the lack of reactivity of diphenylphosphonyl azide with benzene and xylene. Under similar conditions, sulfonyl azides react to form sulfoanilides.<sup>55</sup> This difference in apparent reactivity may involve stabilization of the intermediate by electron delocalization as shown for IXa and IXb so that a higher activation energy would be necessary for reaction.



In this connection it appears that diphenylphosphonyl azide is considerably more stable thermally than benzenesulfonyl azide. The two forms of diphenylphosphonimidotriphenylphosphorane shown as energetically equivalent (VIIIa and VIIIb) would actually be expected to have different potential energies. It is possible that VIIIa, being a higher energy form is capable of existence provided that the potential energy barrier necessary for conversion to the thermodynamically more stable VIIIb is not exceeded. This might account for the low-melting (150°C.) and high-melting forms (170-171°C.) of diphenylphosphonimidotriphenylphosphorane referred to above. It is also possible that diphenylphosphonimidotriphenylphosphorane can exist in two energetically different geometric isomers; models show that there is possible restricted rotation about the phosphorus-nitrogen single bond due to the phenyl groups.

Examination of the infrared spectra of the diarylphosphonyl azides and the diarylphosphonimidophosphoranes shows two absorptions of interest which are common to both classes of compounds. The absorption at



about  $1180\text{ cm}^{-1}$  in the phosphoranes and at about  $1250\text{ cm}^{-1}$  in the phosphonyl azides has been assigned to the P=O absorption. For comparison, triphenylphosphine oxide absorbs at  $1190\text{ cm}^{-1}$ .<sup>56</sup> The second absorption of even more interest is that at  $1316$  to  $1212\text{ cm}^{-1}$  in the phosphoranes and at about  $1258\text{ cm}^{-1}$  in the azides. These absorptions have been assigned to a P=N absorption, in accord with similar absorptions in phosphonitrilic chloride trimer and tetramer<sup>57</sup> in diphenylphosphinic nitride trimer and tetramer, and in the recently reported sulfonimidophosphoranes.<sup>53</sup> The P=O and P=N absorptions for the compounds studied are given in Table XVII.

The ultraviolet spectra of the phosphonyl azides and phosphoranes have been determined using ethanol or acetonitrile as the solvent. The phosphoranes show greatly enhanced aromatic absorptions at  $264\text{-}5$  and  $266\text{-}7\text{ m}\mu$  ( $\log \epsilon$  3.2, 3.5) and at about  $224\text{-}5\text{ m}\mu$  ( $\log \epsilon > 4.5$ ). Diphenylthiophosphonimido-triphenylphosphorane exhibits enhanced aromatic absorptions ( $\log \epsilon$  3.7, 3.85) at the same wavelengths as the oxygen analog and triphenylphosphine sulfide also exhibits a similar enhancement of the aromatic absorptions compared to triphenylphosphine oxide. Diphenylphosphonyl azide has an ultraviolet spectrum similar to that of the phosphoranes.

#### k. Applications

Two interesting applications for the phosphonyl azides and phosphoranes have been briefly investigated. Firstly, the addition of diphenylphosphonimidotriphenylphosphorane to epoxy resins appears to impart useful fire retardant properties, and secondly, if the phosphorane is prepared in situ, the nitrogen gas liberated effectively acts as a blowing agent for the preparation of epoxy foams.

### 2. Boron-Nitrogen Chemistry

The reaction of 3,3',4,4'-tetraaminobiphenyl with benzene-1,3-, and benzene-1,4-diboronic acids and with tetra-n-butyl benzene-1,4-diboronate has been reported previously.<sup>58</sup> The tetrabutyl ester was formed in situ, and it appeared that some protodeboronation occurred because benzene was observed as a reaction product.<sup>59</sup> The polymeric borimidazoles previously obtained appeared to have some intermediate degree of polymerization, or were mixtures of polymer with unreacted benzenediboronic acid and/or tetraaminobiphenyl. It has been found that tetrabutyl benzene-1,4-diboronate prepared and purified prior to reaction with tetraaminobiphenyl appears to yield a purer polymeric product. However, analysis still indicated some intermediate degree of polymerization and/or the presence of some unreacted starting materials. It was found that most of the impurities could be removed by extraction with hot water and hot methanol.

Previous polymerizations were run in toluene. In an attempt to insure a higher degree of polymerization, tetraaminobiphenyl and benzene-1,4-diboronic acid were allowed to react in a thermally stable, high-boiling polar solvent, N,N-didecyl-p-phenoxyaniline. The crude polymer again appeared to have some intermediate degree of polymerization.



TABLE XVII

Infrared Assignments

Compound	P=O Frequency, cm <sup>-1</sup>	P=N Frequency, cm <sup>-1</sup>
$(\text{C}_6\text{H}_5)_3\text{PO}$	1190	--
$(\text{C}_6\text{H}_5)_2\overset{\text{O}}{\underset{\uparrow}{\text{P}}}-\text{N}=\text{P}(\text{C}_6\text{H}_5)_3$	1167	1316, 1302
$(p\text{-CH}_3\text{C}_6\text{H}_4)_2\overset{\text{O}}{\underset{\uparrow}{\text{P}}}-\text{N}=\text{P}(\text{C}_6\text{H}_5)_3$	1170	1227
$(p\text{-ClC}_6\text{H}_4)_2\overset{\text{O}}{\underset{\uparrow}{\text{P}}}-\text{N}=\text{P}(\text{C}_6\text{H}_5)_3$	1176	1239
$(\text{C}_6\text{H}_5)_2\overset{\text{S}}{\underset{\uparrow}{\text{P}}}-\text{N}=\text{P}(\text{C}_6\text{H}_5)_3$	--	1230
$(\text{C}_6\text{H}_5)_2\overset{\text{O}}{\underset{\uparrow}{\text{P}}}-\text{N}=\text{P}(\text{C}_6\text{H}_4\text{-}p\text{-Cl})_3$	1170	1212
$(\text{C}_6\text{H}_5)_2\overset{\text{O}}{\underset{\uparrow}{\text{P}}}-\text{N}=\text{P}(\text{C}_6\text{H}_4\text{-}p\text{-CH}_3)_3$	1176	1266
$(\text{C}_6\text{H}_5)_2\overset{\text{O}}{\underset{\uparrow}{\text{P}}}-\text{N}=\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5$	1170	1250
$(\text{C}_6\text{H}_5)_2\overset{\text{O}}{\underset{\uparrow}{\text{P}}}-\text{N}_3$	1229	1263
$(\text{C}_6\text{H}_5)_2\overset{\text{S}}{\underset{\uparrow}{\text{P}}}-\text{N}_3$	--	1255
$(p\text{-Cl-C}_6\text{H}_4)_2\overset{\text{O}}{\underset{\uparrow}{\text{P}}}-\text{N}_3$	1227	1258



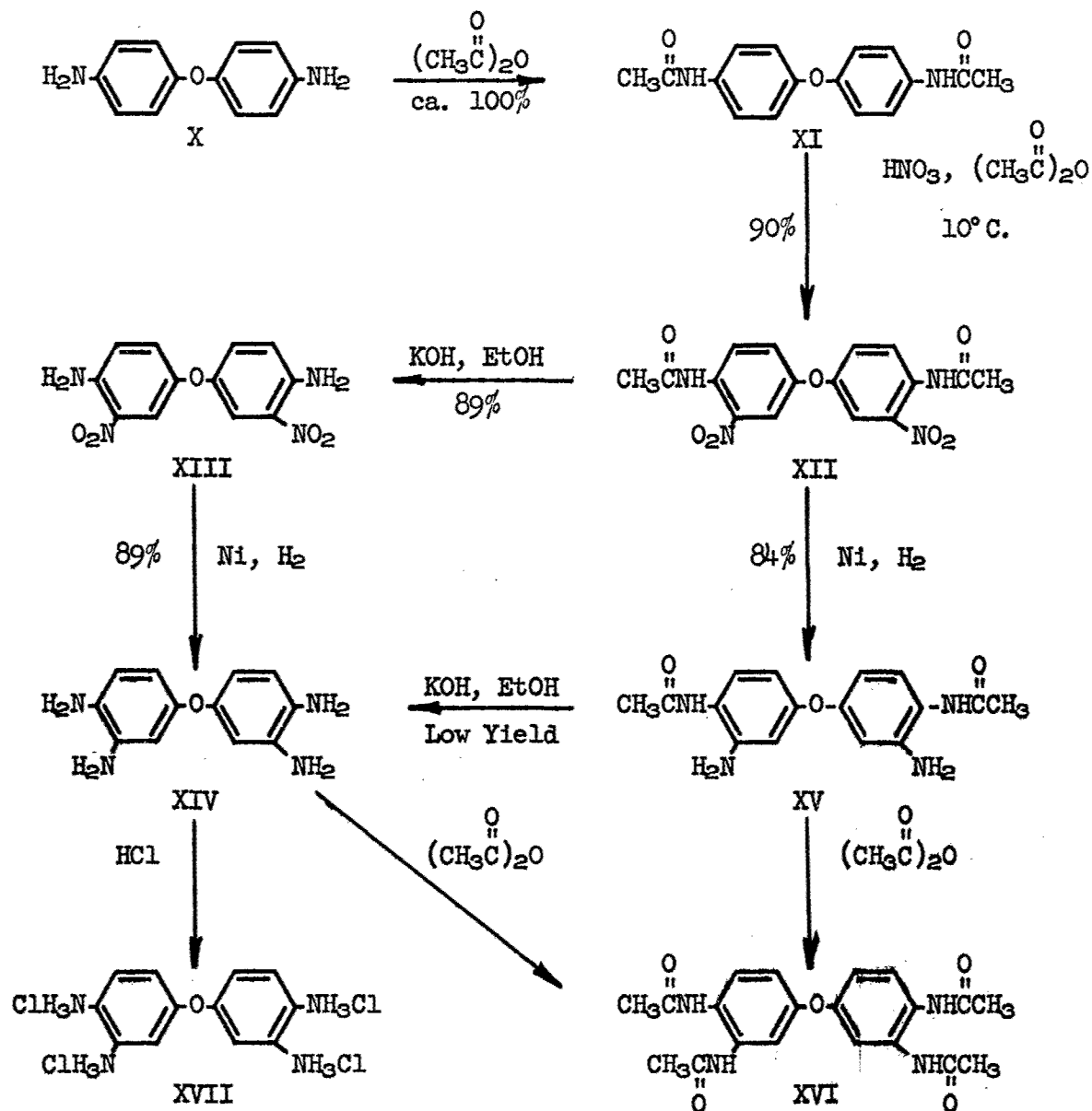
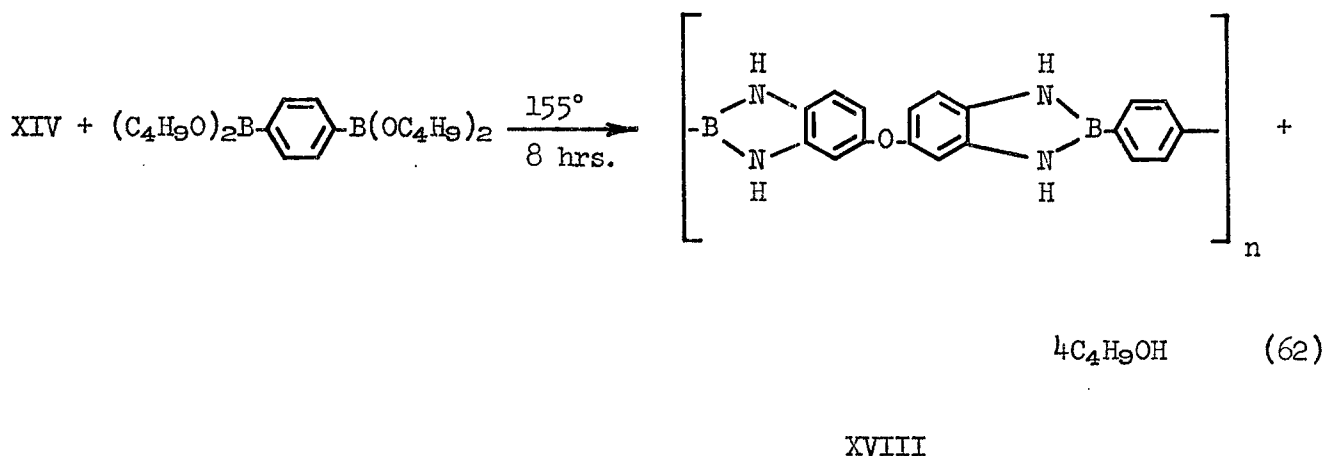


Figure 4. Preparation of 3,3',4,4'-Tetraaminodiphenyl Ether



To prepare a more tractable polymer, a polyamine containing an ether linkage was desired. Therefore, 3,3',4,4'-tetraaminodiphenyl ether (XIV) was synthesized as shown in Figure 4. All steps proceeded readily when each intermediate was purified by recrystallization to give 3,3'-diamino-4,4'-diacetylaminodiphenyl ether (XV) in 76% over-all yield. However, deacetylation of XV to give XIV proceeded in poor yield. Therefore, 3,3'-dinitro-4,4'-diacetylaminodiphenyl ether (XII) was deacetylated and the resultant 3,3'-dinitro-4,4'-diaminodiphenyl ether (XII) reduced to give XIV. This latter route to XIV eliminated the vigorous reaction conditions necessary to deacetylate XV. The tetraamine, XV, was characterized by conversion to the tetraacetate, XVI, and the tetrahydrochloride, XVII.

Although purified XIII was reduced readily over Raney nickel in ethyl acetate, attempted reduction of nonrecrystallized XIII under the same conditions was unsuccessful. However, by using a glacial acetic acid slurry of crude XIII and platinum oxide catalyst, reduction occurred in 1-3 hrs. In contrast, no reduction occurred using platinum oxide in ethyl acetate or diglyme. These results suggest that the catalyst is poisoned by traces of basic potassium compounds in crude XIII. Tetraaminodiphenyl ether, XIV, reacted with tetra-*n*-butyl benzene-1,4-diboronate at 155°C. to liberate 90% of the theoretical butanol based on Equation 62 and produced the new ether-linked borimidazole polymer, XVIII.



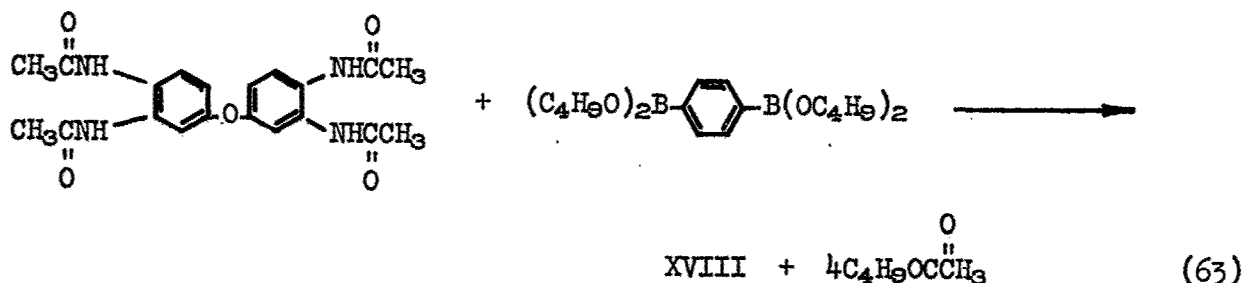
The grey-colored polymer (XVIII) obtained from the interaction of crude 3,3',4,4'-tetraaminodiphenyl ether and crude tetrabutyl benzenediboronate was soluble in both dimethylformamide and dimethylsulfoxide to yield dark red-colored solutions. The grey-colored polymer (XVIII) became brown when washed with hot water and hot methanol. Although there was a 5.4% weight loss when washed XVIII was heated at 300°C./1 mm., there was no other observable change. The infrared spectra of the unwashed, washed, and of the heated XVIII were all similar. The spectrum of the washed and heated XVIII exhibited the most well-defined infrared absorptions. The intrinsic viscosity of the methanol-washed polymer was 0.908, while that of the washed and heated material was 0.900 (in dimethylformamide). The solubility of the polymer also appeared to



change little after the heating, although the rate of solution in dimethylformamide and dimethylsulfoxide was somewhat less. Qualitatively, the borimidazole polymer, XVIII, appeared to have about the same appearance, solubilities, and thermal stability as the borimidazole polymer previously prepared from tetraaminobiphenyl.

A comparison of the major infrared spectral absorptions of the two borimidazole polymers is shown in Table XVIII. The absorption data indicate that the two polymers have the same structural features, and that polymer XVIII has the expected aryl ether absorption at 1242  $\text{cm}^{-1}$ .

Since 3,3',4,4'-tetraacetylaminodiphenyl ether XVI is more easily obtained pure than the tetra-amine XIV, it was hoped that the acetyl derivative would react directly with a benzenediboronic acid ester. When such a reaction was attempted, however, (Equation 63) a 6.3% yield of two, unidentified products was obtained: a carbonaceous-appearing material having a melting point greater than 300°C., and a yellow glass melting at 290-298°C.



### 3. Silicon-Oxygen Chemistry

A 288 g. quantity of the siloxy-carboxylate polymer has been prepared for evaluation of the physical and chemical properties by the method previously reported<sup>60</sup> from diphenyldiacetoxysilane and terphthaloyl chloride as shown in Equation 64.

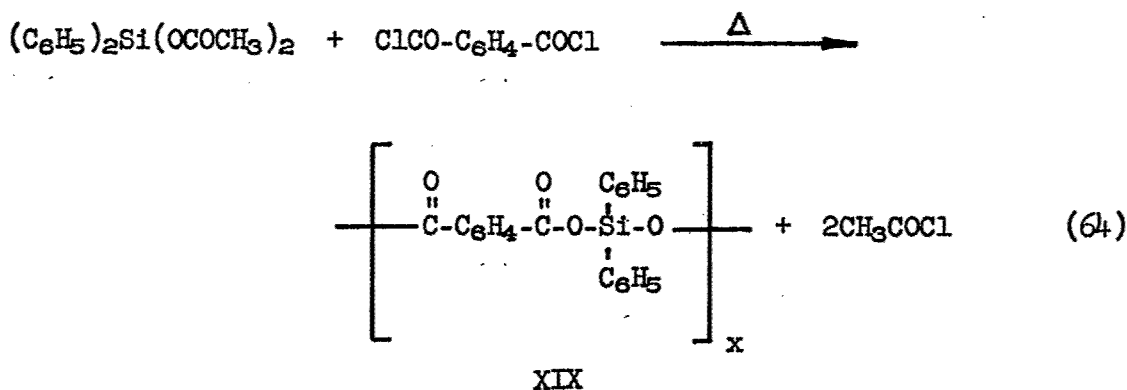




TABLE XVIII

Comparison of Infrared Spectral Absorptions Observed in  
 Borimidazole Polymers Prepared from 3,3',4,4'-Tetraaminobiphenyl,  
 3,3',4,4'-Tetraaminodiphenyl Ether and Benzene-1,4-diboronic Acid

Biphenyl Polymer (1377-115) Frequency, cm <sup>-1</sup>	Diphenyl Ether Polymer (1377-153) Frequency, cm <sup>-1</sup>	Tentative Assignment
3509	3509	N-H
1613, 1484	1600, 1484	C=C Aryl skeletal in-plane vibrations.
1524, 1488	1520(sh)1488	B-N, B-aryl
1360	1360	B-N
1266	1266	
--	1242	=C-O-aryl ether
1163	1156	Aromatic substitution band
1093	1105	B-N
1010	1010	Aromatic substitution band
	966	Present in tetraamino- diphenyl ether
881	--	Present in tetraaminobiphenyl
873	866(sh)	Aromatic substitution band
856	851	" " "
820-802	816(sh) 797	" " "
760	766-759	" " "



## B. Experimental

### 1. Phosphorus-Nitrogen Chemistry

#### a. Phenyldimethylaminophosphonyl Chloride (1134-167, 180)

Dimethylamine (45 g., 1.0 mole), was added as a gas to a mixture of 195 g. (1.0 mole) of phenylphosphonyl dichloride ( $n_D^{20}$  1.5592) and 101 g. (1.0 mole) of triethylamine in 200 ml. of toluene. After stirring overnight, the triethylamine hydrochloride was removed by filtration in an argon atmosphere. The solvent was removed from the filtrate by distillation at 20 mm. at ambient temperature. The dark-colored liquid residue was then fractionated to yield two fractions: (1) b.p. 68-75°C./0.3 mm.,  $n_D^{20}$  1.5580-1.5590; 46.6 g. (0.239 mole), 23.9% recovery of crude phenylphosphonyl dichloride. Anal. calcd. for  $C_6H_5Cl_2OP$ : P, 15.89; Cl, 36.37; Cl:P, 2.00. Found: P, 15.9; Cl, 35.3; N, 0.59; Cl:P, 1.94. (2) b.p. 99-105°C./0.3 mm.,  $n_D^{20}$  1.5469-1.5474; 95.7 g. (0.47 mole), 61.8% yield of phenyldimethylaminophosphonyl chloride based on consumed phenylphosphonyl dichloride. Anal. calcd. for  $C_6H_{11}ClNOP$ : Cl, 17.41; N, 6.88; P, 15.21; Cl:P, 1.00. Found: Cl, 17.02; N, 6.75; P, 14.7; Cl:P, 1.01.

In a second experiment, 195 g. (1.0 mole) of phenylphosphonyl dichloride was allowed to react with 90.2 g. (2.0 moles) of dimethylamine in 300 ml. of toluene. The dimethylamine hydrochloride was removed by filtration and the solvent was removed from the filtrate at reduced pressure to yield a yellow liquid residue. Distillation yielded 159.8 g. (0.785 mole, 78.5% yield) of colorless phenyldimethylaminophosphonyl chloride, b.p. 102-103°C./0.3 mm.,  $n_D^{20}$  1.5472. Anal. Found: Cl, 17.5; P, 15.3; Cl:P, 0.999.

#### b. Diphenylphosphonamide (1134-104)

Gaseous ammonia was slowly bubbled into 71.5 g. (0.30 mole) of diphenylphosphonyl chloride dissolved in 325 ml. of toluene (dried over calcium hydride) at -78°C. The reaction was exothermic. Precipitated solid was removed by filtration, washed with 200 ml. of water, 100 ml. of concentrated ammonium hydroxide, and additional water to yield 56.7 g. of diphenylphosphonamide, m.p. 149-153°C. An analytical sample recrystallized from toluene had a melting point of 154-155°C. Anal. calcd. for  $C_{12}H_{12}NOP$ : C, 66.35; H, 5.57; N, 6.45; P, 14.26. Found: C, 66.08; H, 5.69; N, 6.34; P, 14.3.

#### c. Bis-(p-chlorophenyl)phosphonic Acid

##### (1) Using Diethylaminophosphonyldichloride (1134-19)

The Grignard reagent prepared from 191 g. (1.00 mole) of p-bromochlorobenzene and 24.3 g. (1.00 mole) of magnesium turnings in 1500 ml. of ether was treated with 95 g. (0.50 mole) of diethylaminophosphonyldichloride at such a rate that gentle reflux was maintained. After 2.5 hrs. the thick, milky reaction mixture was hydrolyzed by the addition of 300 ml. of saturated ammonium chloride solution followed by 500 ml. of water. The ether layer was decanted and the water layer was extracted with 500 ml. of ether. The ether was removed by distillation from the combined extracts to yield a yellow solid mass. The solid was treated with 400 ml. of concentrated hydrochloric



acid and the mixture heated under reflux for 4 hrs. A yellow oil was obtained which failed to crystallize on cooling. The oil was dissolved in 5N sodium hydroxide, filtered to remove some solid, and the filtrate acidified with concentrated hydrochloric acid to reprecipitate the yellow oil. The oil was washed with water causing it to solidify. The solid was recrystallized (with difficulty) from ethanol-water to obtain 32.1 g. (0.112 mole, 22.4% yield) of bis(p-chlorophenyl)phosphonic acid, m.p. 136-138°C.; reported<sup>61</sup>, m.p. 133-135°C.

(2) Using Phosphorus Oxychloride (1134-20)

The addition of the Grignard solution prepared from 191 g. (1.00 mole) of p-bromochlorobenzene and 24.3 g. (1.00 mole) of magnesium turnings in 1000 ml. of ether was added to 76.7 g. (0.50 mole) of phosphorus oxychloride dissolved in 1200 ml. of ether during 3.5 hrs. After stirring for 1 hr. in an ice bath and for 2 hrs. at room temperature, hydrolysis was effected by adding 300 ml. of saturated ammonium chloride solution and 500 ml. of water. The two phases which resulted were separated and the aqueous layer basified with 5N sodium hydroxide. A gel was formed which was filtered. No precipitate was observed on acidification of the filtrate. The ether layer yielded an orange-colored, semi-solid on removal of the solvent. Treatment of the orange solid with sodium hydroxide, filtration and acidification of the filtrate with concentrated hydrochloric acid yielded 57.8 g. (0.20 mole, 40% yield) of bis-(p-chlorophenyl)phosphonic acid. A 1 g. quantity of tris-(p-chlorophenyl)-phosphine oxide, m.p. 174-175°C., reported<sup>62</sup>, m.p. 175°C. was recovered from the base insoluble material.

d. Bis-(p-chlorophenyl)-phosphonyl Chloride (1134-24)

A 78.6 g. (0.274 mole) quantity of bis-(p-chlorophenyl)phosphonic acid was allowed to stand with 40 ml. (0.558 mole) of thionyl chloride for 24 hrs. and then an additional 15 ml. of thionyl chloride was added; the mixture was heated under reflux for 2.5 hrs. The excess thionyl chloride was removed at 76°C. and the residue distilled, b.p. 183-187°/0.2 mm., reported<sup>63</sup>, b.p. 280°C./25 mm.) to yield 71.8 g. (0.235 mole, 85.8%) of a pale yellow oil which solidified on standing. Anal. calcd. for  $C_{12}H_8Cl_3OP$ : Cl, 34.82. Found: Cl, 34.6. A sample was sublimed at 100°C. and  $10^{-4}$  mm. to yield a white solid which melted at 69-70°C. and had a Neumayer molecular weight of 306.8 in benzene (theory 305.5).

e. Diphenylthiophosphonyl Chloride (1134-25, 81)

A mixture containing 750 ml. of sodium dried benzene and 220.5 g. (1.00 mole) of diphenylchlorophosphine was warmed to reflux in an argon atmosphere before the first small portion of 32.1 g. (1.00 mole) powdered sulfur was introduced. Succeeding portions of sulfur were added to the mixture maintained at reflux as the sulfur was consumed. After stirring overnight, the benzene was removed by distillation from the bright, yellow-colored solution through a 12-in. Vigreux column. Distillation of the dark-colored residue at 0.15 mm. yielded 246.1 g. (0.974 mole, 97.4%) of bright, yellow-colored diphenylthiophosphonyl chloride boiling at 142-146°C. (reported 155-160°C./0.3 mm.<sup>64</sup>



275-280°C./15 mm.<sup>65</sup>),  $n_D^{20}$  1.6589. Anal. calcd. for  $C_{12}H_{10}ClPS$ : Cl, 14.03; P, 12.26; S, 12.69; M.W., 252.7. Found: Cl, 14.20; P, 12.4; S, 12.8; M.W., 251.6. Acidification of a base soluble portion of the distilland, yielded diphenylthiophosphonic acid, m.p. 137-139°C., after treatment with Norite A (reported,<sup>64</sup> 141-142°C.).

A mixture of 7.12 g. (0.0282 mole) diphenylthiophosphonyl chloride and 5.5 ml. (0.0604 mole) of freshly distilled aniline in 20 ml. of ether was heated under reflux for 24 hrs. The resulting white precipitate was removed by filtration and washed with water to yield 2.78 g. of product. An additional 5.51 g. of product was recovered from the ether layer to give a combined weight of 8.29 g. (0.0268 mole, 95%) of diphenylthiophosphonyl anilide, m.p., 157-158.5°C. Anal. calcd. for  $C_{18}H_{16}NPS$ : N, 4.53; P, 10.01; S, 10.37. Found: N, 4.36; P, 10.2; S, 10.2.

f. Diarylphosphonyl Azides

(1) Diphenylphosphonyl Azide (1134-73,117,168)

(a) Preparation

In several runs diphenylphosphonyl azide was prepared by stirring equimolar quantities of diphenylphosphonyl chloride and sodium azide in pyridine for 24 hrs. at room temperature. The solids were removed from the reaction mixture by filtration. The solvent was removed from the filtrate at reduced pressure at ambient temperatures. The yield of crude, yellow-to-orange colored diphenylphosphonyl azide varied from 93-100%. Distillation of a 1 g. sample at  $10^{-4}$  mm. in a simple bulb-to-bulb apparatus yielded diphenylphosphonyl azide as a colorless, mobile liquid  $n_D^{20}$  1.6077.

(b) Reactions

[1] With Aniline (1134-21-1)

Under an atmosphere of argon, 5.0 ml. (0.055 mole) of aniline was added dropwise to 4.8 g. (0.20 mole) of diphenylphosphonyl azide to yield 4.0 g. (0.014 mole, 70%) of diphenylphosphonanilide, m.p. 241-243°C. (reported<sup>66</sup> 242-244°C.), after recrystallization from ethanol (Norite).

[2] With Water (1134-21-2)

The reaction of 3.5 ml. of water with 0.5572 g. (0.00237 mole) of diphenylphosphonyl azide yielded 0.5166 g. (0.00236 mole, 99.9%) of diphenylphosphonic acid, m.p. 194-196°C., mixture melting point with an authentic sample, 194-196°C.

[3] With Isopropyl Alcohol (1134-22,38)

A mixture of 2.85 g. (0.0117 mole) of diphenylphosphonyl azide, 3.93 g. (5.0 ml., 0.0654 mole) of isopropyl alcohol (dried by



distillation from calcium hydride) and 3.61 g. (5 ml., 0.0357 mole) of triethylamine was heated on a steam bath for 1 hr. and then allowed to stand overnight. After removal of the solvent at reduced pressure, the pale-yellow solid was recrystallized from ethanol-water to give 2.65 g. (0.0101 mole, 86.6%) of isopropyl diphenylphosphonate, m.p. 97.5-98.5°C. (reported<sup>67</sup> m.p. 95-96°C.), having a molecular weight of 261.4 (calcd. 260.3).

[4] With Boron Trifluoride Etherate (1134-80)

A 5.0 g. (0.0205 mole) quantity of diphenylphosphonyl azide in 10 ml. of ether and 2.5 g. (0.037 mole) of boron trifluoride dissolved in 10 ml. of ether were allowed to reflux in a system arranged for the collection of nitrogen. No nitrogen was observed after 48 hrs. and the heating was discontinued. Infrared analysis of the reaction mixture indicated that no reaction had occurred.

[5] Attempted Free Radical Reactions of Diphenylphosphonyl Azide (1134-112,113)

A catalytic quantity of azo-bis-isobutyronitrile was placed in 20 ml. of benzene. The mixture was brought to reflux and then 3.4 g. (0.14 mole) of diphenylphosphonyl azide dissolved in 15 ml. of benzene was added. Since only 30 cc. of gas was liberated, a second small quantity of catalyst was added. After 24 hrs. at reflux, no further gas evolution was observed and the experiment was discontinued.

In a similar experiment, 2.43 g. (0.01 mole) of diphenylphosphonyl azide was heated under reflux in 25 ml. of p-xylene with a small quantity of azo-bis-isobutyronitrile for 24 hrs. without the liberation of nitrogen. After removal of the solvent, an infrared examination of the residual liquid showed a strong azide absorption at  $4.65 \mu$  and no evidence of N-H absorption.

(c) Stability Tests on Diphenylphosphonyl Azide (1134-117,136)

A 23.8 g. (0.10 mole) quantity of crude diphenylphosphonyl azide was stored in a closed system attached to a gas collecting system. After two weeks, there had been no decomposition as evidenced by lack of gas evolution.

Similarly, 2.1 g. of diphenylphosphonyl azide was stored in contact with a strip of No. 316 stainless steel. After three weeks, no decomposition had been observed. There was no evidence of any decomposition of distilled diphenylphosphonyl azide on storage in a sealed ampoule during eight months.

(2) Bis-(p-chlorophenyl)phosphonyl Azide (1134-60)

The interaction of 7.5 g. (0.025 mole) of bis-(p-chlorophenyl)-phosphonyl chloride and 2 g. (0.031 mole) of sodium azide, yielded after the



usual work-up and distillation at  $10^{-5}$  mm. in 2-4 g. lots, 6.3 g. (0.020 mole, 80.8%) of colorless, mobile bis-(p-chlorophenyl)phosphonyl azide,  $n_D^{20}$  1.6246, which was hydrolyzed with difficulty in 0.5N sodium hydroxide. Anal. calcd. for  $C_{12}H_8Cl_2N_3OP$ : Cl, 22.72; N, 13.46; P, 9.93; M.W. 312.1. Found: Cl, 22.65; N, 13.90; P, 9.75; M.W., 324.7.

(3) Bis-(p-tolyl)phosphonyl Azide (1134-23,27)

Under an atmosphere of argon, 14.9 g. (0.056 mole) of bis-(p-tolyl)phosphonyl chloride and 5.0 g. (0.077 mole) of sodium azide in 40 ml. of pyridine were stirred at room temperature for two days. The solids were removed from the reaction mixture by filtration under argon and the solvent was removed by evaporation at ambient temperature at about 1 mm. The liquid residue was submitted to distillation at  $10^{-5}$  mm. but before distillation began, a slow decomposition set in causing a pressure rise to 0.5 mm. However, yellow distillate, b.p. 190-195°C./0.5 mm., which weighed 8.5 g. (0.0313 mole, 56%) was obtained. A portion of the distillate solidified to a cream-colored solid when placed in a  $-78^\circ\text{C}$ . bath. About 1 g. of the distillate was redistilled at  $10^{-5}$  mm. in a small bulb-to-bulb distillation apparatus attached directly to the high vacuum line to yield a mobile colorless liquid. Anal. calcd. for  $C_{14}H_{14}N_3OP$ : N, 15.49; P, 11.42; M.W. 271.25. Found: N, 15.48; P, 11.5; M.W. 272.0.

(4) Diphenylthiophosphonyl Azide (1134-39,41, 73-2)

Following the same general procedure used for diphenylphosphonyl azide, (vide supra) 16.5 g. (0.065 mole) of diphenylthiophosphonyl chloride and 4.5 g. (0.069 mole) sodium azide in 20 ml. of pyridine yielded a pale, yellow liquid residue after removal of the solvent. The liquid became red when it was submitted to distillation through a short column. The red distillate which weighed 12.4 g. (0.048 mole, 73.8% yield) lightened in color to orange after standing for several days. Anal. calcd. for  $C_{12}H_{10}N_3PS$ : N, 16.21; P, 11.95; S, 12.37; M.W. 259.3. Found: N, 14.10; P, 11.90; S, 12.24; M.W. 264.4.

Hydrolysis of the azide in 0.5N sodium hydroxide was extremely slow at either room temperature or on a steam bath but it could be completed on boiling the mixture. This behavior is in contrast to the more facile hydrolysis of diphenylphosphonyl azide at room temperature on standing overnight.

g. Preparation of Phosphoranes from Azides

(1) Bis-(p-tolyl)phosphonimidotriphenylphosphorane (1134-30)

In a system arranged for the collection of nitrogen by water displacement, 3.3 g. (0.012 mole) of bis-(p-tolyl)phosphonyl azide in 8 ml. of ether was added to 3.14 g. (0.012 mole) of triphenylphosphine in 25 ml. of ether at reflux. The evolution of nitrogen was slow and only about 71% complete. The resulting white solid, m.p. 168-178°C., was removed by filtration, washed with ether and with dilute ammonium hydroxide solution and dried at 2.5 mm. for 4 hrs. to yield 3.3 g. (0.0065 mole, 54.4%) of bis-(p-tolyl)phosphonimido-



triphenylphosphorane, m.p. 176-8°C. Anal. calcd. for  $C_{32}H_{29}NOP_2$ : C, 76.02; H, 5.78; N, 2.77; P, 12.26; M.W. 505.52. Found: C, 76.44; H, 5.87; N, 2.79; P, 12.41; M.W. 503.6.

(2) Diphenylthiophosphonimidotriphenylphosphorane (1134-40, 73-3,88)

Since a mixture of 2.3 g. (0.0089 mole) of triphenylphosphine and 2.3 g. (0.0089 mole) of diphenylthiophosphonyl azide in 25 ml. of ether at reflux liberated nitrogen only slowly, 25 ml. of benzene was added to displace the ether. After heating under reflux for 4 hrs., 3 ml. of pyridine was added and the mixture heated under reflux for an additional 30 min. before the solvent was removed at reduced pressure to yield a pale, yellow-colored solid. After a wash with ether and with dilute ammonium hydroxide, the then white solid was digested with isopropyl alcohol yielding 3 g. (0.0061 mole, 68.2%) of diphenylthiophosphonimidotriphenylphosphorane, m.p. 171-172°C., which on recrystallization from ethyl acetate-ethanol and then from ethanol provided a material melting at 179-179.5°C. Anal. calcd. for  $C_{30}H_{35}NP_2S$ : C, 73.00; H, 5.105; N, 2.84; P, 12.54; S, 6.50; M.W. 493.5. Found: C, 73.10; H, 5.14; N, 2.82; P, 12.5; S, 6.33; M.W. 500.7.

When pyridine alone was used as the reaction solvent, the yield of the phosphorane was 91%.

(3) Diphenylphosphonimidotris(p-chlorophenyl)phosphorane (1134-79)

A 3.6 g. (0.0148 mole) quantity of diphenylphosphonyl azide was added to 5.5 g. (0.015 mole) of tris(p-chlorophenyl)phosphine in 25 ml. of pyridine heated under reflux. The evolution of nitrogen, about 350 cc. (theory 332 cc.), was complete in 45 min. Removal of the solvent by distillation gave a cream-colored solid which was washed with dilute ammonium hydroxide and with ether to give 8.6 g. (0.0148 mole, 100% yield) of crude, white diphenylphosphonimidotris(p-chlorophenyl)phosphorane. Further washings and recrystallizations failed to give a sharp melting point, m.p. 135-140°C. Anal. calcd. for  $C_{30}H_{22}Cl_3NOP_2$ : P, 10.67; M.W., 580.8. Found: P, 10.5; M.W. 585.

(4) Diphenylphosphonimidophenyldimethylphosphorane<sup>69</sup> (1134-111)

To a 3.7 g. (0.0152 mole) quantity of diphenylphosphonyl azide dissolved in 20 ml. of pyridine was slowly added 2.1 g. (0.0152 mole) of phenyldimethylphosphine<sup>69</sup> dissolved in 20 ml. of pyridine. The reaction was very exothermic at room temperature but could be controlled by cooling to 0°C. The nitrogen evolved was 88.2% of theory. Removal of the solvent at reduced pressures yielded 3.6 g. (67% yield) of a white solid, m.r. 125-145°C., which was insoluble in ether and in dilute ammonium hydroxide solution. A sample recrystallized from isopropyl alcohol-water mixture oiled and then solidified to yield a powder, m.p. 155-157°C. Calc. M.W., 353; Found: M.W. 372.



h. Attempted Preparation of Diphenylphosphonimidotriphenylphosphorane from Diphenylphosphonamide (1134-105)

Chlorine gas was bubbled into a solution of 13.1 g. (0.05 mole) of triphenylphosphine in 125 ml. of carbon tetrachloride until a yellow gum precipitated. The mixture was aspirated briefly and excess triethylamine added. Solid diphenylphosphonyl amide (10.8 g., 0.05 mole) was added to the mixture. After standing in a closed system for 60 hrs., the brown mixture was concentrated at reduced pressure to yield a brown-colored solid which was washed with ether and ammonium hydroxide. None of the desired diphenylphosphonimidotriphenylphosphorane was obtained.

i. In Situ Process for Phosphorane Syntheses

(1) General Procedure

In this procedure, equal molar quantities of sodium azide and a tertiary phosphine were mixed, under dry argon, and brought to gentle reflux and then the chloride in pyridine or other solvent was added at such a rate that a gentle evolution of nitrogen was maintained. The evolved gas was collected by water displacement, and was used as a measure of phosphorane formation. The results of a number of survey reactions are shown in Table XVI.

(2) In Situ Preparation of Bis-(p-chlorophenyl)-phosphonimidotriphenylphosphorane (1134-69)

A 1.0 g. (0.015 mole) quantity of sodium azide and 3.4 g. (0.011 mole) of bis-(p-chlorophenyl)phosphonyl chloride were warmed almost to reflux in 25 ml. of pyridine before 2.9 g. (0.011 mole) of triphenylphosphine in 15 ml. of pyridine was added at such a rate that a steady evolution of nitrogen was maintained. Although only about 67% of the theoretical nitrogen was collected, 4.5 g. (0.0082 mole, 74.5%) of white powder was obtained after ether and dilute ammonium hydroxide washes; m.p. 205-208°C. Anal. calcd. for  $C_{30}H_{23}Cl_2NOP_2$ : C, 65.94; H, 4.24; Cl, 12.98; N, 2.56; P, 11.34; M.W. 546.4. Found: C, 65.89; H, 4.30; Cl, 12.8; N, 2.40; P, 10.8; M.W., 552.

(3) In Situ Preparation of Diphenylphosphonimidotriphenylphosphorane

(a) In Pyridine Solvent (1134-44, 83, 103, 106)

A mixture of 2.2 g. (0.034 mole) of sodium azide and 7.87 g. (0.033 mole) of diphenylphosphonyl chloride in 25 ml. of dry pyridine was stirred at room temperature for 1.5 hrs. before being brought almost to reflux at which point addition of 8.73 g. (0.033 mole) of triphenylphosphine in 20 ml. of pyridine resulted in the evolution of 600 cc. of nitrogen in 10 min. and a total of about 630 cc. (about 84.4%) after 1 hr. After the usual work-up, 12.4 g. (0.026 mole, 78.8%) of the phosphorane, m.p. 151-152°C. was obtained.

Following the same procedure, 236.5 g. (1.00 mole) of diphenylphosphonyl chloride and 65 g. (1.0 mole) sodium azide in 700 ml. of



pyridine were stirred under argon for 48 hrs. at room temperature. The mixture was then warmed almost to reflux and 262 g. (1.00 mole) of triphenylphosphine (recrystallized from isopropyl alcohol and Norite A) was added during 3 hrs.

The solvent was removed at reduced pressure to yield a pink solid which was slurried with 2 lbs. of ether. A sample withdrawn at this point, washed with ether, dilute ammonium hydroxide, and water, had a melting point of 150-151°C. However, after the main portion of the solid was removed by filtration and allowed to stand for two days, the solid, 465 g., 0.974 mole, 97.4% yield, was found to have a melting point of 164-167°C. A sample washed with ether and then with ammonium hydroxide solution had a melting point of 168-170°C. which was raised to 170-171°C. by recrystallization from isopropyl alcohol-water mixture. Anal. calcd. for  $C_{30}H_{25}NOP_2$ : C, 75.46; H, 5.28; N, 2.93; P, 12.98; M.W., 477.5. Found: C, 75.63; H, 5.47; N, 2.92; P, 13.0; M.W., 481. The infrared spectrum of the higher melting product was similar to the lower melting form in a potassium bromide pellet except for small shifts in some of the principal absorption bands. When the two forms were dissolved in carbon disulfide, the resulting infrared and ultraviolet spectra were identical.

A redetermination of the infrared absorption spectrum of an earlier sample, m.p. 150-152°C., which now melted over the range 147-168°C., did not show any shift toward the spectrum of the higher melting material. However, recrystallization from isopropyl alcohol-water gave the product with the higher melting point and the shifted infrared spectrum.

Two other attempts to prepare the lower melting material were carried out in pyridine and in ether as solvents. The yields were 97.5% and 88.0%, respectively, of the higher melting material with the shifted spectrum.

(b) In Dimethylformamide Solvent (1134-77, 147, 162)

A 1.0 g. (0.015 mole) quantity of sodium azide and 2.6 g. (0.01 mole) of triphenylphosphine were mixed in 20 ml. of dry dimethylformamide and warmed almost to reflux before the addition of 2.4 g. (0.01 mole) of diphenylphosphonyl chloride was begun. The addition was completed in 15 min. with a quantitative evolution of nitrogen and the formation of a precipitate. After removal of the solvent at reduced pressure ( $< 1$  mm.), the resulting cream-colored solid was washed with two 25 ml. portions of ether, 25 ml. dilute ammonium hydroxide solution, and dried at reduced pressure for 8 hrs. to give 3.8 g. (79.5%, 0.00795 mole) of diphenylphosphonimidotriphenylphosphorane, m.p. 151-152°C. having a molecular weight of 480 (calcd. 477.5).

In a second experiment, 0.65 g. (0.01 mole) of sodium azide in 20 ml. of dimethylformamide (dried over calcium hydride) was slowly added to 2.4 g. (0.01 mole) of diphenylphosphonyl chloride dissolved in 10 ml. of dimethylformamide. The initial evolution of gas was slow but increased as the mixture was brought to reflux. After approximately 250 cc. (theory 224 cc.) of gas had been collected by water displacement, the addition of 2.6 g. (0.01 mole) of triphenylphosphine in 5 ml. of dimethylformamide caused the vigorous evolution of an additional 250 cc. of gas. On cooling, the mixture solidified



to a brown mass with an amine-like odor; litmus indicated the presence of base.

Solvent was removed at reduced pressure, and the resulting solid was washed with 50 ml. of ether, 50 ml. of dilute ammonium hydroxide and 50 ml. of water to give 2.5 g. (0.0052 mole) of light tan, crude diphenylphosphonimidotriphenylphosphorane. Acidification of the basic wash with hydrochloric acid yielded about 1.1 g. (0.005 mole) of crude diphenylphosphonic acid.

When diphenylphosphonyl azide was placed in dimethylformamide which had been dried over anhydrous sodium sulfate, no gas was evolved during one week.

j. Anomalous In Situ Reaction:  
Formation of Diphenylphosphinic Nitride (1134-85)

The addition of a 25 ml. portion of a 253 g. (1.00 mole, 205 ml.) quantity of diphenylthiophosphonyl chloride to a hot mixture of 65 g. (1.0 mole) of sodium azide and 262 g. (1.00 mole) of triphenylphosphine (recrystallized from isopropyl alcohol and Norite) in pyridine resulted in little nitrogen evolution until the mixture was heated under reflux. After all of the diphenylthiophosphonyl chloride had been added (6 hrs.), the reaction mixture was heated and stirred for an additional 36 hrs. while nitrogen slowly evolved. The resulting mixture was filtered through a sintered glass funnel (under argon) to yield a yellow-white solid and an orange filtrate.

The yellow-white solid was washed with ether and then with water to yield 255 g. of a very pale yellow solid which after recrystallization from n-butyl acetate had a melting point of 160-162°C. Comparison of the infrared spectrum of the unknown with the infrared spectra of diphenylthiophosphonimidotriphenylphosphorane, m.p. 179-179.5°C. and triphenylphosphine sulfide, m.p. 161°C.<sup>70</sup> indicated that the unknown product was triphenylphosphine sulfide and not the expected phosphorane. Anal. calcd. for  $C_{30}H_{25}NP_2S$  (diphenylphosphonimidotriphenylphosphorane): N, 2.84; P, 12.54; S, 12.54; calcd. for  $C_{18}H_{15}PS$  (triphenylphosphine sulfide): P, 10.52; S, 10.89. Found: N, 0.00; P, 10.8; S, 10.9. The yield of triphenylphosphine sulfide was 86.7%.

The orange-colored pyridine filtrate was concentrated at reduced pressure to yield a tacky yellow residue which remained gummy after digestion with isopropyl alcohol. When the gum was dried in high vacuum, a yellow friable, benzene soluble solid was obtained. Attempted recrystallization from benzene, ethanol, and butyl acetate was unsuccessful. When about half of the yellow solid was heated at 275-280°C. in high vacuum, the material refluxed gently. On cooling, a yellow glass formed which was dissolved in a minimum amount of hot benzene. A white solid slowly precipitated from the benzene solution on standing, m.p. 318-320°C. (softens 315°C.). The infrared spectrum was identical with that of diphenylphosphinic nitride tetramer<sup>51,71</sup>. Approximately 16 g. of tetramer was isolated from the viscous yellow gum. This represents a yield of approximately 16% based on diphenylthiophosphonyl chloride.



k. Attempt to React Diphenylthiophosphonimidotriphenylphosphorane and Triphenylphosphine (1134-109)

Under an atmosphere of argon, 1.0 g. (0.002 mole) of diphenylthiophosphonimidotriphenylphosphorane and 0.54 g. (0.002 mole) of triphenylphosphine dissolved in 10 ml. of dry pyridine were heated on a steam bath for 6 hrs. and allowed to stand overnight. After removal of the solvent, 0.95 g. (95% recovery) of crude diphenylthiophosphonimidotriphenylphosphorane, m.p. 174-178°C., was obtained.

In a similar experiment, the reactants were refluxed for 24 hrs. Again, only diphenylthiophosphonimidotriphenylphosphorane, 0.94 g. (94% recovery), m.p. 173-176°C. and triphenylphosphine, 0.45 g. (83% recovery), m.p. 78-80°C. were obtained.

l. Reaction of Triphenylphosphine and Diphenylthiophosphonyl Chloride (1134-148)

To 7.9 g. (0.03 mole) of triphenylphosphine dissolved in 20 ml. of refluxing pyridine was added 7.6 g. (0.03 mole) of diphenylthiophosphonyl chloride. After heating under reflux in an argon atmosphere for 18 hrs., the solvent was removed at reduced pressure yielding a semi-solid. After washing with dilute ammonium hydroxide and digestion with isopropyl alcohol, 8.0 g. (0.027 mole, 91% yield) of triphenylphosphine sulfide, m.p. 158-160°C., was obtained. Acidification of the basic extract with concentrated hydrochloric acid yielded impure diphenylphosphonic acid, m.p. 140-170°C., as indicated by the infrared spectrum of the solid.

m. Attempt to Hydrolyze Diphenylphosphonimidotriphenylphosphorane

(1) With Acid (1134-159)

A mixture containing 30 ml. of 6N sulfuric acid and 4.8 g. (0.01 mole) of diphenylphosphonimidotriphenylphosphorane was heated on a steam bath for 18 hrs. The solids were removed from the mixture by filtration. Basification of the filtrate yielded only a trace of an oily, brown-colored solid. The solids were washed with dilute ammonium hydroxide solution and dried at 100°C. to give a solid having a melting range of 166-169°C. with a trace of solid remaining at 195°C. Acidification of the basic wash yielded no diphenylphosphonic acid. Recrystallization of the solid from isopropyl alcohol-water mixture gave 4.2 g. (0.00838 mole, 83.8% recovery) of diphenylphosphonimidotriphenylphosphorane, m.p. 169-170°C.

(2) With Base (1134-158)

To 4.8 g. (0.01 mole) of diphenylphosphonimidotriphenylphosphorane slurried in 15 ml. of ethanol was added 0.1 g. (0.0025 mole) of sodium hydroxide in 5 ml. of water. The mixture was heated under reflux for 6 hrs. and then stirred for an additional 18 hrs. at room temperature. The solvent was removed at reduced pressure to yield a white solid. The solid was



broken up, washed well with water, and vacuum dried to yield 4.8 g. (100% recovery) of diphenylphosphonimidotriphenylphosphorane, m.p. 169-170°C., mixture m.p. of 169-170°C. with an authentic sample.

n. Applications

(1) Evaluation of Diphenyl-  
phosphonyl Azide as a Blowing Agent (1151-48,49)

Tetraethylenepentamine (2.9 g.) was first mixed thoroughly with 20 g. Epon 828 and then trimethyl phosphite (0.4 g.) and lastly diphenylphosphonyl azide (0.4 g.) was added. Care was taken not to expose the azide for prolonged periods to the atmosphere. There was no apparent nitrogen evolution at room temperature, and therefore the mixture was placed in an oven at 100°C. for 10 min., producing a thermoset resin with uniformly entrapped bubbles. The bulk density of the cured resin was 0.797 g./cc. which represents approximately a 30% reduction.

In a second test, the same quantities and mixing procedure were used except that the curing agent consisted of 1.5 g. tetraethylene pentamine and 2.2 g. dibutylethylene diamine. An 18.6 g. quantity of the formula was placed in a suitable container in an oven at 100°C. for 20 min. The resulting rigid, thermoset foam was found to have a density of 0.177 g./cc. representing about an 83% reduction in the density of the amine-cured epoxy.

(2) Evaluation of Diphenylphosphonimido-  
triphenylphosphorane as a Fire Retardant (1151-59)

Diphenylphosphonimidotriphenylphosphorane (2 g.) was dissolved in 4 g. of isopropyl alcohol and mixed with 20 g. of Epon 828. After thorough mixing, the solvent was removed by warming the resin mixture to 70°C. at 2 mm. The mixture was then cooled to room temperature and 2 g. of diethylenetriamine was added. The mixture was thoroughly blended and deaerated under 2 mm. pressure. The resin was cast into a 1/8 in. thick panel and cured for 1 hr. at 80°C.

Using the same procedure, a similar panel was cast without the diphenylphosphonimidotriphenylphosphorane to use as a standard.

A 4 x 1/2 in. strip was cut from each panel, i.e., control formula and formula containing the phosphorane. The two strips were clamped on a ring stand and a 1 in. high Bunsen flame applied for 15 sec., then removed. The control sample ignited and burned vigorously for 2 min., at which time the fire had to be extinguished, having consumed from 1 to 1-1/2 in. of the original 4 in. piece.

The sample containing the phosphorane did not ignite on the first application of flame for 15 sec.; on the second application of the Bunsen flame the sample ignited and burned for 90 sec. before extinguishing itself after consuming only 1/8 to 1/4 in. of the original 4 in. piece. A third application of flame for 15 sec. again caused ignition and the sample burned for 55 sec., extinguishing itself again with no further appreciable consumption of material.



## 2. Boron-Nitrogen Chemistry

### a. n-Butyl Borate (1134-114,124)

The reaction of excess n-butyl alcohol with boric anhydride<sup>72</sup> provided 5200 g. (22.58 moles, 94.1% yield) of n-butyl borate, b.p. 119-123°C./21 mm., based on the boric anhydride.

### b. Tetra-n-butyl Benzene-1,4-diboronate (1134-125,132,135)

A solution of 14.7 g. (0.10 mole) of p-dichlorobenzene in 150 ml. of n-butyl borate was slowly added to 9.2 g. (0.40 mole) of sodium dispersed in 200 ml. of n-butyl borate at 102°C. at a rate sufficient to maintain the reaction temperature at 102-110°C. for about the first half of the addition. The first drop of p-dichlorobenzene solution caused immediate formation of a purple color. The second half of the addition was carried out at 60-90°C. with the temperature being brought back to 100°C. at the end of the addition. After stirring at room temperature for 30 min., the mixture was cooled to 20°C. and of 7.8 g. (0.0667 mole) of boron trichloride was added with some temperature increase (20-26°C.).

The purple-colored mixture was pressure-transferred through a sintered glass funnel to yield a yellow filtrate. The purple solids were washed out of the reaction flask with petroleum ether (b.r. 20-40°C.). The solids retained on the funnel were quite active toward water and alcohols. Distillation of the liquid at about 0.1-0.2 mm. yielded 26.6 g. of n-butyl borate containing p-dichlorobenzene, b.p. up to 58°C., and 211 g. of tributyl borate, b.p. 56-58°C. Infrared analysis of the brown viscous residue (7 g., ca. 18% yield) indicated that it was essentially pure tetra-n-butyl benzene-1,4-diboronate.

In a second experiment the same procedure was used except that the addition of the p-dichlorobenzene was carried out at 104-114°C. The initially formed purple color changed to a brown. The mixture was stirred at 100°C. for 20 min. after the addition of the p-dichlorobenzene was complete. After 30 mins. stirring at room temperature, the mixture was cooled to 20°C. and boron trichloride passed into the mixture which caused the brown color to change again to purple. The mixture became too viscous to stir and, therefore, 150 ml. of petroleum ether (b.r. 20-40°C.) was added. The reaction mixture was filtered as described above. Distillation of the yellow filtrate yielded little forerun and 210 g. (about 70% recovery) of n-butyl borate, b.p. 48-52°C./0.2 mm. The brown residual liquid weighed 14.3 g. and was shown by infrared analysis to be essentially pure tetrabutyl benzene-1,4-diboronate. (ca. 22% yield).

### c. Preparation of 4,4'-diacetyl-aminodiphenyl Ether (XI) (1377-89; 1134-115,119)

4,4'-Diaminodiphenyl ether (7.95 g., 0.0398 mole) was heated on a steam bath for 30 min. with 100 ml. of a 1:1 mixture of acetic anhydride-acetic acid. The reaction mixture was poured onto ice. The solids were removed



by filtration washed with water and recrystallized from acetic acid to give 11.3 g. (0.0398 mole, 100%) of 4,4'-diacetylaminodiphenyl ether, m.p. 225-227°C. Anal. calcd. for  $C_{16}H_{16}N_2O_3$ : N, 9.86. Found: N, 9.42 (Kjeldahl).

In a second run, acetic anhydride (410 g., 4.00 moles) was slowly added to 400 g. (2.00 moles) of 4,4'-diaminodiphenyl ether in 450 ml. of glacial acetic acid with stirring and cooling. After being stirred and heated at 100°C. for an additional 1.5 hrs., the purple-brown colored suspension was poured onto 1 Kg. of ice. The solids were removed by filtration and washed with 200 ml. of water, 500 ml. of dilute ammonium hydroxide solution and an additional 500 ml. of water to yield 534.4 g. (1.88 mole, 94% yield) of purple-colored 4,4'-diacetylaminodiphenyl ether, m.p. 215-220°C.

A third preparation on the same scale but run at 50°C. throughout the addition of the acetic anhydride and at higher dilution by the use of an additional 700 ml. of glacial acetic acid resulted in a quantitative yield of tan-colored 4,4'-diacetylaminodiphenyl ether, m.p. 222-225°C.

d. Preparation of 3,3'-Dinitro-4,4'-diacetylaminodiphenyl Ether (XII) (1377-93, 113; 1134-116, 121)

A 5.0 g. (0.018 mole) quantity of 4,4'-diacetylaminodiphenyl ether was added to acetyl nitrate prepared from 6.75 g. 70% nitric acid and 40 ml. acetic anhydride according to the procedure of Bordwell and Garbisch<sup>73</sup>. The reaction mixture was stirred at 10-15°C. for 30 min. after the addition and then poured into ice water. The resulting solids were removed by filtration, washed with ice water and then with petroleum ether, and air dried to give 6.0 g. (0.016 mole, 89%) of 3,3'-dinitro-4,4'-diacetylaminodiphenyl ether as yellow needles, m.p. 200-202°C., after crystallization from acetic acid and then from ethanol. Anal. calcd. for  $C_{16}H_{14}N_4O_7$ :  $NO_2$ , 24.58. Found:  $NO_2$ , 24.43 (Titanous chloride reduction). Treatment with acetic anhydride, then crystallization from ethanol and, finally, recrystallization from ethyl acetate raised the melting point to 215-215.5°C.

In a second run, a 301 g. (1.06 moles) quantity of 4,4'-diacetylaminodiphenyl ether was suspended in 600 ml. of acetic anhydride and slowly added to acetyl nitrate (381 ml. of 70% nitric acid and 2800 ml. of acetic anhydride) at such a rate that the reaction temperature could be maintained at 10-15°C. with an ice-salt bath. After the addition was complete, the mixture was stirred for 30 min. at 10-15°C. The yellow-colored suspension was poured onto 2 Kg. of ice. The mixture quickly generated excessive heat causing some loss of product and the development of an orange color. Filtration yielded an orange-red colored solid which was washed with ethyl acetate to yield 239.3 g. (0.639 mole, 60.3% yield) of bright yellow-colored 3,3'-dinitro-4,4'-diacetylaminodiphenyl ether, m.p. 212-215°C.

A third preparation on the same scale and using the same procedure except for more careful cooling in the hydrolysis step yielded 351.5 g. (0.939 mole, 88.6% yield) of bright yellow-colored 3,3'-dinitro-4,4'-diacetylaminodiphenyl ether, m.p. 211-214°C.



e. Preparation of 3,3'-Diamino-4,4'-diacetylaminodiphenyl Ether (XV) (1377-117,119)

In a preliminary experiment, 2.0 g. (0.0053 mole) of purified 3,3'-dinitro-4,4'-diacetylaminodiphenyl ether was reduced at 60 psig hydrogen pressure over Raney nickel in ethanol to give 1.5 g. (0.0048 mole, 91%) 3,3'-diamino-4,4'-diacetylaminodiphenyl ether as white plates from ethanol, m.p. 213-214°C.

In a similar manner, 75 g. (0.20 mole) of purified 3,3'-dinitro-4,4'-diacetylaminodiphenyl ether was reduced in an autoclave at 200 psig hydrogen pressure to give 52.7 g. (0.17 mole, 84%) of 3,3'-diamino-4,4'-diacetylaminodiphenyl ether, m.p. 213-213.5°C., from ethanol. Anal. calcd. for  $C_{16}H_{18}N_4O_3$ : N, 17.83;  $NH_2$ , 10.20. Found: N, 16.47 (Dumas);  $NH_2$ , 9.34 (nonaqueous titration);  $NO_2$ , 0.43 (Titanous chloride reduction).

f. Preparation of 3,3'-dinitro-4,4'-diaminodiphenyl Ether (XIII) (1377-142; 1134-121)

A solution of 3,3'-dinitro-4,4'-diacetylaminodiphenyl ether (3.3 g., 0.0088 mole) in 53 ml. ethanol was treated with 1.02 g. (0.0182 mole) potassium hydroxide in 25 ml. distilled water and heated on the steam bath until a clear red solution obtained (5 min.). The solution was cooled and 1.8 g. of a red crystalline solid was removed by filtration, m.p. 176-177°C. Recrystallization from ethyl acetate gave 1.6 g. (0.0056 mole, 63.3%) of 3,3'-dinitro-4,4'-diaminodiphenyl ether as a red, microcrystalline powder, m.p. 178.5-179°C. Anal. calcd. for  $C_{12}H_{10}N_4O_5$ : C, 49.66; H, 3.47. Found: C, 50.06; H, 3.70.

A further 0.4 g. (15.8%) of product was obtained by filtration of the partially evaporated ethanolic filtrate and recrystallization of the solid from ethyl acetate, m.p. 178-179°C.

In a similar manner a slurry of 591 g. (1.58 moles) of 3,3'-dinitro-4,4'-diacetylaminodiphenyl ether in 2.5 l. of methanol was slowly treated with 177 g. (3.16 moles) of potassium hydroxide dissolved in 700 ml. of methanol over a 30 min. period. The reaction mixture was stirred for 2 hrs. and then poured into 2 l. of distilled water. After filtration, water washing, and drying, the red-colored, finely crystalline 3,3'-dinitro-4,4'-diaminodiphenyl ether, m.p. 173-175°C., weighed 440.5 g. (1.52 moles, 96.1% yield).

g. Preparation of 3,3',4,4'-Tetraaminodiphenyl Ether (XIV) (1377-143; 1134-152,153,155)

3,3'-Dinitro-4,4'-diaminodiphenyl ether (2.0 g., 0.0068 mole) dissolved in 200 ml. ethanol was reduced over Raney nickel at 37 psig hydrogen pressure. The catalyst was removed by filtration and the solvent removed by evaporation on a Rinco evaporator. The resulting crude solid (1.4 g., 0.00607 mole, 89.2%) was recrystallized from ethanol and from ethyl acetate in an argon atmosphere to yield 3,3',4,4'-tetraaminodiphenyl ether, m.p. 120-122°C. The product was colorless when first prepared but turned dark within a few minutes when exposed to light. The product was converted to the tetrahydrochloride for



analysis. Anal. calcd. for  $C_{12}H_{18}N_4Cl_4O$ : C, 38.31; H, 4.82. Found: C, 38.93; H, 5.62.

In a second run, 14.5 g. (0.05 mole) 3,3'-dinitro-4,4'-diaminodiphenyl ether (crude) was slurried with 200 ml. of glacial acetic acid and 0.1 g. of platinum oxide and reduced at an initial hydrogen pressure of about 45 psig. The reduction was complete in 1-3 hrs. at ambient temperature to yield a dark-green solution. After removal of the catalyst by filtration under argon, the solution was concentrated at reduced pressure to a thick, dark-green residue which was used without further purification for preparation of the polymer (vide infra). When the reduction was attempted in ethyl acetate with Raney nickel, no pressure drop was observed. Similar nonreactivity was obtained using platinum oxide in ethyl acetate and diglyme.

h. Preparation of 3,3',4,4'-Tetracetylaminodiphenyl Ether (XVI) (1377-122)

Approximately 0.25 g. (0.00060 mole) 3,3'-diamino-4,4'-diacetylaminodiphenyl ether was acetylated by warming with 20 ml. acetic anhydride on a steam bath to give 0.1 g. (0.00025 mole, 42%) of 3,3',4,4'-tetracetylaminodiphenyl ether as a white powder, m.p. 222-226°C., after washing with water and recrystallization from acetic acid. Anal. calcd. for  $C_{20}H_{22}N_4O_5$ : N, 14.42. Found: N, 13.57 (Dumas); 14.7 (Kjeldahl).

i. Biphenyl-Borimidazole Polymer

(1) Purification (1377-114)

A 6 g. quantity of impure borimidazole polymer prepared from tetra-n-butylbenzene-1,4-diboronate and 3,3',4,4'-tetraaminobiphenyl analyzing C, 67.76; H, 5.46; B, 4.46; N, 16.73 was triturated with hot water (80-90°C.). The remaining solids were removed by filtration, dried for 12 hrs. at 100°C./0.5 mm., and reanalyzed. Found: C, 69.28; H, 5.86; B, 4.58; N, 16.89.

The filtrate deposited brown needles which were removed by filtration, vacuum dried (100°C./0.5 mm.) and analyzed. Found: C, 64.49; H, 5.59; N, 21.66. The elemental analysis and infrared spectrum indicated that the solid was a mixture of benzene-1,4-diboronic acid and 3,3',4,4'-tetraaminobiphenyl. A second crop of needles, obtained when the filtrate was cooled was treated as described above. Found: C, 62.40; H, 6.78; N, 23.55. These data and the infrared spectrum indicated that this solid was mainly 3,3',4,4'-tetraaminobiphenyl.

(2) Preparation without Solvent (1377-115)

A mixture of tetra-n-butyl benzene-1,4-diboronate (1.21 g., 0.0031 mole) and 3,3',4,4'-tetraaminobiphenyl was heated to the melting point of the tetraamine (180°C.) and held there until the evolution of n-butanol (0.7 g., 78.7%) ceased. The temperature of the reaction mixture was then raised to and maintained at 250°C. for 3 hrs. The resulting 1.25 g. of grey-tan solids were ground in a mortar and analyzed. Anal. calcd. for  $C_{18}H_{14}B_2N_4$ : C, 70.20;



H, 6.78; B, 7.02; N, 18.19. Found: C, 60.33; H, 4.75; B, 9.80; N, 10.43.

Approximately 0.5 g. of this material was triturated with hot methanol and filtered. The resulting solid (0.15 g.) was dried at 100°C./0.5 mm. and reanalyzed. Found: C, 69.07; H, 5.14; B, 6.10; N, 18.41.

The methanol filtrate was evaporated to dryness and the resultant solid (0.3 g.) analyzed. Found: C, 53.26; H, 5.49; B, 10.10; N, 2.67. The elemental analyses and infrared spectrum indicated that the extracted material was mainly benzene-1,4-diboronic acid.

(3) Preparation in N,N-didecyl-  
p-phenoxyaniline (1377-92)

A mixture of 6.21 g., (0.015 mole) tetra-n-butyl benzene-1,4-diboronate and 3.2 g. (0.015 mole) of 3,3',4,4'-tetraaminobiphenyl were heated at 250°C. in 30 ml. of N,N-didecyl-p-phenoxyaniline for 4 hrs. releasing 4.0 g. (91%) of n-butanol. The resulting solid was removed by filtration, washed with petroleum ether (b.r. 30-60°C.) and air dried. Anal. calcd. for  $C_{18}H_{14}B_2N_4$ ; C, 70.20; H, 6.78; B, 7.02; N, 18.19. Found: C, 71.85; H, 6.78; B, 4.44; N, 12.0.

j. Diphenyl Ether-Borimidazole  
Polymer (XVIII) (1377-150; 1134-156,157,166)

When a mixture of tetra-n-butyl benzene-1,4-diboronate (2.20 g., 0.00564 mole plus 0.22 g. excess) and 3,3',4,4'-tetraaminodiphenyl ether (1.3 g., 0.00564 mole) was heated 8 hrs. at 155°C., 1.5 g. n-butanol (0.0202 mole, 89.8% was removed by distillation. The mixture was then heated at 260°C./0.1 mm. for 18 hrs. The remaining solid was collected and washed with petroleum ether (30-60°C.), and dried to yield 2.4 g. of crude polymer. Part of the crude material (0.5 g.) was triturated with hot ethanol and the resulting solid (0.4 g.) was then vacuum-dried 18 hrs. at 100°C./0.3 mm.; m.p. > 375°C. Anal. calcd. for  $C_{18}H_{14}B_2N_4O$ : C, 66.72; H, 4.36; N, 17.29. Found: C, 65.87; H, 4.64; N, 17.22.

In a second experiment, approximately 26.2 g. (0.114 mole) of crude 3,3',4,4'-tetraaminodiphenyl ether (see above) was allowed to react with 44.4 g. (0.114 mole) of crude tetra-n-butyl benzene-1,4-diboronate to yield a purple slurry. Xylene (150 ml.) was added and the mixture distilled until the head temperature reached 110°C. (75 ml. of distillate). After standing overnight, a purple solid was removed from the slurry by filtration. When the purple solid was vacuum dried (ambient temp./1 mm., 18 hrs.), 39.4 g. of a grey powder was obtained. The infrared spectrum of this material was similar to that of previous preparations of the polymer. A sample of this powder which had been washed with methanol was found to have an intrinsic viscosity of 0.908 in dimethylformamide.

Attempted purification of 29.3 g. of the grey powder was carried out by first washing with two 125 ml. portions of hot water and then with 150 ml. of hot methanol. A few crystals which were recovered from the water wash had an infrared spectrum of benzene-1,4-diboronic acid. A 6.899 g. portion of the



washed product was further heated at 240-293°C./1 mm. for 0.5 hr. and then at 293-310°C./1 mm. for 2.5 hrs. with the loss of a small amount of water and acetic acid identified by infrared analysis. The infrared spectrum of this fraction was again similar to all previous spectra although it is a much sharper spectrum. The recovery of polymer was 94.6%. Heat treatment of the polymer did not appear to effect the infrared spectrum or the intrinsic viscosity (0.900 in dimethylformamide) to any great extent. Anal. calcd. for  $C_{18}H_{14}B_2N_4O$ : C, 66.72; H, 4.36; N, 17.29; B, 6.61. Found: C, 67.02; H, 4.60; N, variable; B, 5.49.

In a third experiment, about 2.9 g. (0.0126 mole) of crude 3,3',4,4'-tetraaminodiphenyl ether and 4.4 g. of tetra-n-butyl benzene-1,4-diboronate were mixed to give at first a green, then a grey suspension. All volatiles were removed and the powder was refluxed in 30 ml. of xylene for 8 hrs. The solvent was removed, the powder washed with hot methanol and dried at 100°C./1 mm. The brown solid (4.4 g.) had an infrared spectrum similar to that of the previous preparation. Anal. calcd. for  $C_{18}H_{14}B_2N_4O$ ; C, 66.72; H, 4.36; N, 17.29; B, 6.67. Found: C, 66.53; H, 5.00; N, 17.25; B, 5.37.

### 3. Silicon-Oxygen Chemistry

#### a. Preparation of Silicon-carboxylate Polymer (XIX) (1134-98)

To a slurry of 174 g. (0.86 mole) of terphthaloyl chloride in 400 ml. of dry p-xylene in a 1 l. resin flask was added a 50 g. portion of 259 g. (0.86 mole) of diphenyldiacetoxysilane. The resulting solution was stirred at room temperature for 30 min. before the remainder of the silane and an additional 100 ml. of p-xylene were added. Acetyl chloride and p-xylene were removed by distillation up to a head temperature of 70°C. and then the pressure was reduced to about 20 mm. The pressure was then reduced to 2 mm. and heat applied for 4 hrs. at such a rate that the polymer remained fluid. On cooling, a dark-brown glass formed which was readily broken out of the flask, and pulverized in a mortar. A residual odor of acetyl chloride was removed by pumping the powdered polymer at 0.3 mm. for 18 hrs. The yield of a brittle, brown-colored glass was 288 g.



## V. SUMMARY AND CONCLUSIONS

A glass cloth reinforced laminate was prepared using poly-P-methylsesquimethyleneborophane resin which had too low a heat distortion temperature for high temperature applications. The resin obtained from the adduct of methyl- $\beta$ -hydroxyethylphosphine and diborane was too unstable oxidatively and hydrolytically to merit more than cursory study.

A series of linear P-methyl-n-alkylborophane polymers was prepared together with the by-product triborophanes to evaluate the effect of alkyl chain length on the properties of the polymers. P-(3,3-Dimethylcyclotrimethylene)borophane polymer was prepared to test the effect of CPC bond angle on degree of polymerization and although the small angle appears to promote linear polymer formation this conclusion will require verification. Additional data supporting an "unzipping" type of depolymerization for the linear borophane polymers was obtained.

The stereoisomers of 1,3,5-trimethyl-1,3,5-triphenyl- and 1,3,5-trineopentyl-1,3,5-triphenyltriborophanes have been separated by fractional crystallization. The oxidative stabilities of the latter triborophane and P-hexaneopentyltriborophane were determined but no increase in stability due to the presence of the neopentyl group was observed. Syntheses of triborophanes which are substituted with reactive functional groups on either boron or phosphorus have been achieved. A B-cyano substituent appears to increase oxidative stability.

Several new phosphine borines and organo-phosphines were prepared for use as intermediates.

Some new approaches to thermally stable polymers were screened based on BN,  $\overset{\text{O}}{\parallel}\text{SiOC}$ , and PN bonding systems. New borimidazole polymers based on 3,3',4,4'-tetraaminodiphenyl ether and benzenediboronic acids and new polymers based on diphenyldihydroxysilane and terphthalic acid were prepared.

Several members of two new classes of compounds, phosphorus azides and phosphoranes, were prepared and characterized. Diarylphosphonyl azides have remarkable thermal stability and can be distilled. The azides react with trivalent phosphorus compounds to yield phosphoranes. The phosphoranes investigated appeared to have excellent hydrolytic, thermal, and oxidative stability. For example, diphenylphosphonimidotriphenylphosphorane did not autoignite in air at 450°C. and appeared to be thermally stable above about 400°C. (DTA), and it was not hydrolyzed by 6N sulfuric acid during 18 hrs. at 100°C. or by boiling alcoholic sodium hydroxide.



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## APPENDIX I. CHEMISTRY OF INORGANIC POLYMER COMPONENTS

### I. Infrared Spectroscopy of Phosphinoborine Trimers

Early in the history of the  $(R_2PBH_2)_3$  compounds it was considered that B-H bonding electrons probably maintain some interaction with the adjacent phosphorus 3d orbitals, thus strengthening the bonding around the six-atomic ring and decreasing the hydridic character of the hydrogen on boron. This effect would also strengthen the ring-bonding because the P-B dative bond polarity would be partially compensated. The idea seemed to gain support from the X-ray crystallographic determination of the molecular structure of  $[(CH_3)_2PBH_2]_3$  by W. C. Hamilton,<sup>1</sup> indicating the HBH bond angle to be  $119.3^\circ$ . Since the PBP bond angle was surely determined as near  $112^\circ$ , the HBH angle should have been less than  $109^\circ$  if there were no B-H to  $P_3d$  interaction. However, X-ray diffraction is lacking in accuracy for hydrogen in molecules having atoms with much higher nuclear charges (such as phosphorus), so that the wide HBH bond angle could not be taken as final. Hence independent study by infrared spectroscopy seemed valuable for a better understanding of this type of polymer bonding.

The hypothesis of B-H to  $P_3d$  interaction would predict wider HBH bond angles with increasingly electronegative groups on phosphorus, because the  $P_3d$  orbitals would contract and so become more effective for receiving electrons from the B-H bonds. Thus  $CF_3$ -P phosphinoborine trimers would be well worthy of structural study, such as would be even more difficult by the X-ray method as far as hydrogen is concerned. Accordingly, we now have recorded new infrared spectra for  $[(CH_3)_2PBH_2]_3$ ,  $[(CH_3)_2PBD_2]_3$ ,  $(CH_3CF_3PBH_2)_3$ ,  $[(CF_3)_2PBH_2]_3$ , and  $[(CF_3)_2PBD_2]_3$ , with the analogous  $[(CH_3)_2NBH_2]_3$  for comparison.

The trimer  $(CH_3CF_3PBH_2)_3$  is a new member of this class, obtained in a very slight yield from the unstable borine adduct  $CH_3CF_3PH \cdot BH_3$  and recognized only by its infrared spectrum. For completion of our comparisons, a larger sample will be needed, and the deuterio-analogue  $(CH_3CF_3PBD_2)_3$  also must be made. The other deuterio-analogues were made from an unusually pure sample of  $B_2D_6$ , prepared by our ONR-contract colleague John R. Spielman.

#### A. Chemistry Leading to the Trimer $(CH_3CF_3PBH_2)_3$

1. The Phosphine  $CH_3CF_3PH$ . Methyl-trifluoromethyl-phosphine was made conveniently by a reasonably fast room-temperature reaction between  $PH_3$  and  $CH_3CF_3PI$ , the latter of which had been made as described earlier (Ref. 2, page 174). A 0.630 mmole sample of the iodophosphine, left overnight in a sealed tube with 1.493 mmoles of  $PH_3$ , produced 0.206 mmole (35% yield) of  $CH_3CF_3PH$ , with recovery of 0.282 mmole of  $PH_3$ .

The product was combined with another sample of presumed  $CH_3CF_3PH$  from an earlier synthesis using the  $CH_3PH_2$ - $CF_3I$  method (Ref. 2, page 179), after their infrared spectra had proved to be virtually identical. The combined sample was purified by high-vacuum fractional condensation (passing  $-100^\circ$  and condensing at  $-110^\circ$ ), repeated to achieve constant vapor-tension values. The results shown with the equation in Table XIX determine the normal b.p. as  $17.94^\circ C.$  and the Trouton constant as 21.06 cal./deg.mole. The vapor-phase molecular weight (100 mm.,  $25^\circ C.$ ) was determined as 117.0 (calcd., 116.0).



TABLE XIX

Vapor Tensions of CH<sub>3</sub>CF<sub>3</sub>PH

$$(\log P_{\text{mm}} = 5.6331 + 1.75 \log T - 0.0055515T - 1586/T)$$

t (°C.)	-78.5	-64.16	-49.70	-23.60	0.00	18.09
P <sub>mm</sub> (obsd.)	2.55	8.80	25.6	122.4	374	763
P <sub>mm</sub> (calcd.)	2.58	8.80	25.5	122.3	375	763

The final demonstration of the identity of CH<sub>3</sub>CF<sub>3</sub>PH was based upon the infrared spectrum, which very clearly showed the presence of CH<sub>3</sub>, CF<sub>3</sub>, and P-H groups, and included no unexplainable frequencies. Taken with the molecular weight value, these results leave no doubt of the formula CH<sub>3</sub>CF<sub>3</sub>PH.

Five recordings of the spectrum were made by means of the Perkin-Elmer Infracord instrument, using a 10-cm. NaCl cell to contain the vapor. At pressures as low as 2 mm. the C-F stretching frequencies could be observed sharply, and pressures as high as 40 mm. were used to detect very weak bands. The data and interpretations are presented in Table XX.

The low intensities of the C-H stretching bands are usual for hydrocarbon-P-CF<sub>3</sub> compounds, of which we now have more than a dozen showing this effect. Omitted from Table XX were three extremely weak, broad peaks at 1987, 1866, and 1570 cm.<sup>-1</sup>, which might include overtones or combinations, but which are difficult to distinguish from bands for water vapor in the comparison beam.

2. The Phosphine Borine Complex. A 0.463 mmole sample of pure CH<sub>3</sub>CF<sub>3</sub>PH was treated with 0.428 mmole of B<sub>2</sub>H<sub>6</sub>, with slow warming from -78°C. to 22°C. Three hours later the excess B<sub>2</sub>H<sub>6</sub> was recovered by distillation from -78°C. regained, 0.196 mmole; used, 0.232 mmole. Thus the composition of the complex was CH<sub>3</sub>CF<sub>3</sub>PH·1.002BH<sub>3</sub>. It appeared as a mobile but nonvolatile liquid at -78°C. It proved to be stable enough for high-vacuum distillation without dissociation to form any B<sub>2</sub>H<sub>6</sub>, but on standing at 22°C. it approached a dissociation equilibrium, as shown by excessive pressure at 0°C. and a slow decrease of pressure from 4 mm. to 1 mm. at -78°C. (during one minute). Measurement of the equilibrium pressures at three temperatures (4.4 mm. at 0°C., 9.7 mm. at 11.3°C., and 17.5 mm. at 22°C.) gave  $\log P_{\text{mm}} = 8.696 - 2197/T$  (calcd. pressures, 4.5, 9.4, and 17.5 mm.). The Trouton constant, 26.6 cal./deg. mole, is high enough to suggest some dissociation during evaporation.



TABLE XX

Infrared Absorption Frequencies for CH<sub>3</sub>CF<sub>3</sub>PH

Frequency (cm. <sup>-1</sup> ) and character	Interpretation	Frequency and character	Interpretation
2980 w, p 2925 w, p 2820 vvw, p	C-H stretch	1187 vs, sh 1183 vvs, p 1179 vvs, p 1135 vvvs, p	C-F stretch
2360 w, sh	2 x 1180	997 m, p	P-H bending
2320 ms, pp	P-H stretch	900 ms, p	CH <sub>3</sub> rocking
2260 w, p	2 x 1135	841 s, p	CH <sub>3</sub> wagging
1435 m, p	C-H bend, δ-e	742 737	{C-F bend, δ-e P-C stretch
1377 1366	Overtones		
1304 mw, bp 1276 w 1259 w	C-H bend, δ-a	697 m, sh 689 m, p 684 m, sh	{C-F bend, δ-a P-C stretch

Character:

- v - very
- w - weak
- m - medium
- s - strong
- b - broad
- p - sharp peak, judged in relation to frequency
- pp - unusually sharp, narrow peak
- sh - shoulder



3. Decomposition of the Borine Complex. The above sample of  $\text{CH}_3\text{CF}_3\text{PH}\cdot\text{BH}_3$ , held at  $100^\circ\text{C}$ . for 16 hours in a small sealed tube, formed 0.433 mmole of  $\text{H}_2$  (vs. expected 0.463) and liberated 0.080 mmole of nearly pure  $\text{CH}_3\text{CF}_3\text{PH}$ . Evidently some of the  $\text{H}_2$  came from the decomposition of diborane, and accordingly the main product was a water-white nonvolatile oily material, to be understood as an incipient stage of resin-formation. The solid aspect included a very small yield of a slightly volatile product, just barely sublimable under high vacuum at ordinary temperature. Thus its volatility seemed to be intermediate between  $[(\text{CH}_3)_2\text{PBH}_2]_3$  and  $[(\text{CF}_3)_2\text{PBH}_2]_3$ , as expected for the new compound  $(\text{CH}_3\text{CF}_3\text{PBH}_2)_3$ .

The infrared spectrum of this product was not easily recorded, on account of the milligram size of the sample, but it was found possible to coat it upon one window of the cell, thus improving the intensities somewhat. The observed bands, shown in the middle column of Table XXI, clearly accord with the assumption that the material was  $(\text{CH}_3\text{CF}_3\text{PBH}_2)_3$ .

#### B. The Recording of the Spectra

The instruments employed for the infrared spectroscopy were the Beckman IR7 and Perkin-Elmer 13 spectrophotometers, respectively for the regions above 600 and from 800 down to  $400\text{ cm}^{-1}$ , both instruments having high resolving power and good accuracy of frequency measurement. Only vapors of the samples were in the paths of the beams, to avoid interferences offered by liquid or solid phases. For sample pressures as high as 30 mm., required for recording the weaker bands, temperatures up to  $125^\circ\text{C}$ . were necessary. Accordingly, a cell only 7 cm. long was surrounded by heated air; in either of two ways. The first method was to place the cell in a corrugated-paper box having NaCl windows, and lead through the box a stream of hot air from a heater-blower (hair dryer). This method permitted a precise knowledge of the temperature (and therefore the pressure of the sample), but it was not possible to eliminate the water vapor, carbon dioxide, and even hydrocarbon materials. The second method employed a system of small tube furnaces: two of finger size to surround the side-arms of the cell, and two larger ones surrounding the two halves of the cell-body. These latter had such length as to provide a 15-mm. overhang beyond the cell windows, with denser coil-windings for extra heat at the ends. The currents through these furnaces were so adjusted that the side-arms were cooler than the main body of the cell; thus it was possible to calibrate the fingers at fixed voltages, and so have the temperatures governing the sample pressures. Each sample thus had an equilibrium between vapor in the main cell body and solid or liquid in a side-arm. The exception was the tiny sample of  $(\text{CH}_3\text{CF}_3\text{PBH}_2)_3$ , for which all efforts were made to condense the material upon one window. Another exceptional technique was the cooling of a side arm to  $15^\circ\text{C}$ . so that the pressures of the  $[(\text{CF}_3)_2\text{PBH}_2]_3$  and  $[(\text{CF}_3)_2\text{PBD}_2]_3$  vapors would be low enough for good recording of the C-F stretching bands.

With adequate knowledge of the sample pressures, it was possible to calculate the relative absorption coefficients of the various peaks by means of the Beers-Lambert equation  $k = \frac{1}{p} \log \frac{I_0}{I}$ , thus providing an objective basis for comparing the intensities of corresponding bands for analogous substances. For such a comparison to have any value, of course, it was necessary to determine



TABLE XXI

## Infrared Absorption Frequencies of Ring Trimers

Probable Assignment	$[(CH_3)_2PBH_2]_3$	$[(CH_3)_2PBD_2]_3$	$(CH_3CF_3PBH_2)_3$	$[(CF_3)_2PBH_2]_3$	$[(CF_3)_2PBD_2]_3$	$[(CH_3)_2NBH_2]_3$
C-H stretch	2991 m 2925 ms	2992 mw 2928 mw	2970 vw 2940 w	---	---	3045, 3038 3028 vw-w 2990, 2952 m 2902, 2860 w
B-H stretch B-D stretch	2404 vs 2356 s	1807 mw 1743 w	2467 s 2407 ms	2516 mw 2429 w	1889 w 1794 mw	2460 w-sh 2428, 2400, 2324 mw-m
C-F overtone	---	---	2376 w	2310 vw	2304 w	----
B-N stretch	---	---	---	---	---	1236, 1206 ms 1180, 1171 m
C-H bending	1423 mw 1298 m	1423 mw 1295 w	1420 s 1304 ms	---	---	1485 mw 1408 w 1435, 1440 m
C-F stretch	---	---	1191 ss 1149 ss	1205 ss 1192 ss 1164 ss	1205 sss 1192 vss 1164 ss	----
B-H bend, $\delta$ -a B-H bend, $\delta$ -e	1110 mw 1000 mw	892 w 837 vw	1089 ms 1000 m	covered 1151?vs	952 vw 852 vw	1111 w 1032 mw
N-CH <sub>3</sub> stretch	---	---	---	---	---	1068 w
CH <sub>3</sub> rocking	938 vs 853 mw	936 m 852 w	978 w 876 w	---	---	uncertain uncertain
C-P-C asym. stretch	750 m	747 w	754?m	499, 489vw 480, 476vw 452 mw	490 w 440 mw	Bands that could mean CH <sub>3</sub> rock, N-C stretch, or BH <sub>2</sub> wag are
C-P-C symm. str.	unobsd.	unobsd.	unobsd.?	434 mw 414 w	428 w 404 w	998 w 936 m 897 w 850 vw 826 w
C-F bend, $\delta$ -a C-F bend, $\delta$ -e	---	---	765 w unobsd.	763 vw 552 vw	761 vw 565 mw	
P-B-P asymm. str. P-B-P symm. str.	720 ms unobsd.	698 mw unobsd.	667 mw unobsd.	657 m- 617 w	661 m 602 ms	



TABLE XXI-CONTINUED

Probable Assignment	$[(CH_3)_2PBH_2]_3$	$[(CH_3)_2PBD_2]_3$	$(CH_3CF_3PBH_2)_3$	$[(CF_3)_2PBH_2]_3$	$[(CF_3)_2PBD_2]_3$	$[(CH_3)_2NBH_2]_3$
BH <sub>2</sub> wagging	810 w	603 ms	903 ms	995 mw	755 w	uncertain
BH <sub>2</sub> rocking	665 mw	515 w	695 m	711 ms	535 w	uncertain
Unassigned	---	559 w	991 sh 731 vw 652 mw	1040 ww 588 ww 531 vw 524 ww 515 ww	1151 vs 1040 vw 565 mw 524 vw 516 vw	(see above)

(The relative intensities are comparable from column to column, increasing in the order of ww, vw, w, mw, m, ms, s, vs, ss, vss, over a range 1-400; however, middle-column estimates are uncertain because the sample was very small. The C-F stretching frequencies average ten times as intense as vs.)



whether any of the bands might show a wide variation with slit width; accordingly each sample was scanned repeatedly at different slit widths, and the highest intensity was taken as correct for each band. The most extreme variation was found for the  $2356\text{ cm}^{-1}$  band of  $[(\text{CH}_3)_2\text{PBH}_2]_3$ . At the standard slit-width of the IR7 instrument it appeared only as a messy wide and shallow peak or poor shoulder on the  $2402\text{ cm}^{-1}$  band, which remained nearly constant over a wide range of slit widths. At lower slit widths, the  $2356\text{ cm}^{-1}$  band was even less evident, and faded out altogether at half the standard slit-width. But at slit-widths 1.5, 2, 3, 4, and 6 times the standard, this peak became very sharp, with respective intensities 0.25, 0.50, 0.63, 0.68, and 0.67 as high as the  $2402\text{ cm}^{-1}$  band. Another example is the triplet for the highest-frequency C-H stretching band of  $[(\text{CH}_3)_2\text{NBH}_2]_3$  (final column of Table XXI). At standard slit, this was difficult to resolve, but at double and triple slit-width, the three peaks became perfectly distinct.

### C. Interpretation of the Spectra

The main record of the spectra of these trimer-ring compounds is presented by Table XXI, along with the probable assignments. For the highest frequencies these assignments are quite certain, but some ambiguity might have crept into the modes suggested for frequencies below the range of the C-F stretching frequencies. Most useful are the bands assigned to  $\text{BH}_2$  or  $\text{BD}_2$  rocking and wagging, for these strongly indicate an increase of HBH bond angle as  $\text{CF}_3$  is substituted for  $\text{CH}_3$  on P.

1. The C-H and C-F Frequencies. The C-H stretching modes for the phosphino-borine trimers show the normal frequencies corresponding to the symmetric and asymmetric vibrations; for  $(\text{CH}_3\text{CF}_3\text{PBH}_2)_3$  these are definitely weaker than one might expect for half as many methyl groups per molecule - probably because the polarity introduced by the  $\text{CF}_3$  group decreases the possible change of polarity during the C-H stretching vibration. Far less routine is the multiple splitting of the C-H stretching modes of the aminoborine trimer. Here we must recognize the effect of steric interference among the three methyl groups occupying axial positions on the chair-form  $(\text{B-N})_3$  ring. This mutual interference is apparent also in the X-ray structural results,<sup>3</sup> and accounts as well for the splitting of frequencies assigned to C-H bending in this trimer. No such split modes appear for the phosphinoborine trimers, the  $(\text{P-B})_3$  rings are enough flatter to avoid mutual interference by the methyl groups.<sup>1</sup>

The C-F stretching modes have the usual extreme intensities and show the expected multiplicities. The single  $\text{CF}_3$  group per P atom in  $(\text{CH}_3\text{CF}_3\text{PBH}_2)_3$  shows the normal symmetric and asymmetric stretching vibrations, while the  $(\text{CF}_3)_2\text{P}$  units show the usual triplet. It is interesting that deuteration of  $[(\text{CF}_3)_2\text{PBH}_2]_3$  has some effect upon the intensities and contours of the C-F stretching bands, so that a comparison spectrum, taken with the  $\text{BH}_2$  and  $\text{BD}_2$  compounds in the two beams or the IR7 instrument, could not be made to cancel out by adjusting the temperature differential; cancellation of one peak in the C-F stretching region left the other two with resultant peaks or broad bands. For this reason it was not possible to find a possible B-H bending frequency in the C-F stretching region by that method.

The C-F bending frequencies were recognized by analogy to the results of Nabi and Sheppard for a series of considerably simpler  $\text{CF}_3\text{-S}$  compounds.<sup>4</sup> These assignments simplified the task of accounting for other bands in the same general region.



2. Other Modes Involving Carbon. Frequencies not affected by B-deuteration, and corresponding to  $\text{CH}_3$  rocking modes in simpler known compounds, are so assigned in the present study. It is interesting that the  $\text{CH}_3\text{CF}_3\text{P}$  group shows higher  $\text{CH}_3$  rocking frequencies than the  $(\text{CF}_3)_2\text{P}$  group, suggesting stronger bonding of  $\text{CH}_3$  to the more electronegative phosphorus atom. The  $\text{CH}_3$  rocking modes for  $[(\text{CH}_3)_2\text{NBH}_2]_3$  probably are split, and are not easily distinguished from  $\text{BH}_2$  wagging and one of the N-C stretching modes. These N-C stretching modes also may well be complicated by the mutual interference of the methyl groups on one side of the ring, so that the C-N-C symmetric mode would not be symmetrical in fact.

The  $\text{H}_3\text{C-P-CH}_3$  asymmetric stretching modes seem evident enough, but  $\text{H}_3\text{C-P-CF}_3$  asymmetric stretching could be different enough to render the selection of the  $754\text{ cm}^{-1}$  band fairly uncertain. The symmetric  $\text{H}_3\text{C-P-CH}_3$  stretching mode apparently is absent, but this could be explained on the ground that such a mode would involve too small a change of polarity. The analogous  $\text{H}_3\text{C-P-CF}_3$  mode should be split, and it is difficult to select its bands from among the three unassigned frequencies. The  $\text{F}_3\text{C-P-CF}_3$  stretching modes seem to be very complicated, with more and weaker bands for  $[(\text{CF}_3)_2\text{PBH}_2]_3$  than for  $[(\text{CF}_3)_2\text{PBD}_2]_3$ . Some of the extremely weak unassigned bands also may apply here.

3. Skeletal Stretching Modes. In the  $(\text{P-B})_3$  ring we might expect boron to vibrate toward and away from the adjacent P atoms, simultaneously or alternately, giving modes respectively described as symmetric or asymmetric. The former would involve less change of polarity and so is not observed for the  $(\text{CH}_3)_2\text{P}$  compounds, but does seem to be present for the  $(\text{CF}_3)_2\text{P}$  compounds. The difference suggests that  $[(\text{CH}_3)_2\text{PBH}_2]_3$  has much less P-B dative-bond polarity than  $[(\text{CF}_3)_2\text{PBH}_2]_3$ . For the  $(\text{CH}_3\text{CF}_3\text{PBH}_2)_3$  case, however, no decision is yet possible, for lack of the complete spectrum.

The P-B-P asymmetric stretching mode would imply much more change of polarity, and accordingly appears clearly for the methyl compounds. It is notable that deuteration lowers the frequency, as expected if boron is carrying two D instead of two H atoms. The yet lower frequency for the  $\text{CH}_3\text{CF}_3\text{PBH}_2$  trimer may be ascribed partly to weaker ring bonding and also slightly to a less mobile phosphorus atom. However, these effects do not lower the frequencies of the  $(\text{CF}_3)_2\text{P}$  compounds to a similar extent, so that one may wonder whether these are correctly assigned.

The B-N stretching modes for the aminoborane trimer seem to be split, presumably again on account of the interference among the axial methyl groups. They are assigned by reference to other B-N dative-bonded compounds, such as  $(\text{CH}_3)_3\text{NBH}_3$ .<sup>5</sup>

4. The B-H Vibrational Modes. The importance of the HBH bond angles for the understanding of the character of the polymer bonding in the phosphinoboranes makes it especially useful to study all vibrational modes involving B-H bonds. These are easily recognized by comparison with the B-D frequencies, by application of the rule that B-H frequencies normally are about one-third higher than B-D frequencies for corresponding modes. Thus the B-H stretching modes are unmistakable (and show steric splitting in the aminoborane trimer); however the interesting trend toward higher and more separated frequencies as  $\text{CH}_3$  is replaced by  $\text{CF}_3$  on P cannot be ascribed solely to increasing HBH bond angles, for increasing B-H bond



energy would have the same effect. Also the single B-H bending modes are difficult to interpret in relation to the HBH angles, and indeed at least one of these modes is covered by the edge of the region of the extremely intense C-F stretching bands. However, there are BH<sub>2</sub> group modes for which useful interpretations are possible.

Of at least five possible BH<sub>2</sub>-group vibrational modes, we may ignore those involving major motion of the boron atom, for only one of these seems to appear (the P-B-P asymmetric stretching) and none of them would offer much understanding of the role of hydrogen. However, the modes roughly designated as BH<sub>2</sub> rocking and wagging are highly informative.

For the BH<sub>2</sub> rocking motion we think of a circle with a B atom near the center and two H atoms on the rim, along which both H atoms move back and forth without changing the HBH bond angle. This circle defines a plane perpendicular to the P-B-P plane. For wagging, we think of two H atoms on a line which rotates back and forth around a parallel axis, with the boron placed a little beyond this axis. Again there is no change of HBH bond angle or B-H distance. With these pictures we see at once that the radius of wagging is roughly measured by  $r \cos \frac{1}{2}\theta$  (where  $r$  is the distance from H to the center of gyration and  $\theta$  is the bond angle); but for rocking the cosine factor is absent. Thus the shorter-radius wagging frequencies must be higher than the rocking frequencies. Both modes will increase their frequency as the B-H bond energy is increased by the electronegativity effect of CF<sub>3</sub> groups, but the wagging will increase its frequency still more if the bond angle is widened at the same time - whereas the rocking mode will be scarcely affected by the changing bond angle.

Looking now at the data for BH<sub>2</sub> and BD<sub>2</sub> wagging and rocking as given in Table XXI, we find just the trends that would be expected by the theory, if we assume that the HBH (or DBD) bond angle widens and the B-H (B-D) bond energy increases as CF<sub>3</sub> replaces CH<sub>3</sub> on P. Also, it seems very difficult to find any acceptable alternative explanation of the observed frequencies. Hence the indicated structural modification seems quite real, although more and better data for (CH<sub>3</sub>CF<sub>3</sub>PBH<sub>2</sub>)<sub>3</sub> and (CH<sub>3</sub>CF<sub>3</sub>PBD<sub>2</sub>)<sub>3</sub> would be desirable as further evidence.

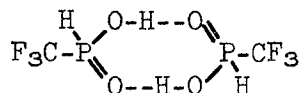
Such a widening of the HBH bond angle by substitution of CF<sub>3</sub> groups for CH<sub>3</sub> on phosphorus would correlate with an increased interaction of B-H bonding electrons with P<sub>3d</sub>, but it could also be suggested that the inductive withdrawal of P-B dative bonding electrons toward phosphorus would have the same HBH bond-widening effect - for an electronic vacancy on the phosphorus side of the boron atom would have to be partly compensated by the B-H bonding electron clouds. It seems beyond doubt that both effects contribute to the widening of the HBH bond angle, but their relative importance cannot be decided without a very thorough quantum-mechanical analysis of such molecules.



## II. Trifluoromethyl-Phosphorus-Oxygen Compounds

### A. The Infrared Spectrum of $(\text{CF}_3\text{HPOOH})_2$

The compound  $\text{CF}_3\text{PO}_2\text{H}_2$  had been indicated to exist almost entirely in the dimer form



with appreciable dissociation to the monomer occurring only above  $100^\circ\text{C}$ . (Ref. 2, page 170). However, the infrared spectrum had been recorded only with the infra-red instrument, with poor control of the temperature and consequent uncertainty of pressure, so that better data were needed for judging the indicated structural pattern. The deficiency now has been amended by the use of the Beckman IR7 instrument, both at the normal  $40^\circ\text{C}$ . temperature of the cell chamber and with the 7-cm. cell in the special box heated as high as  $98^\circ\text{C}$ . Thus pressures of the dimer vapor as high as 20 mm. were employed; and it is calculated that the partial pressure of the monomer vapor then would be 0.12 mm.

The indicated formula was fully confirmed by the results, for the only bands corresponding to O-H stretching were at 2988, 2967, 2930, and  $2857\text{ cm}^{-1}$ , all of medium-weak intensity and assignable to the hydrogen-bridged system. If the vapor at elevated temperatures contained any species other than the dimer and monomer, the previously-reported dissociation data would have required much more than a 0.12 mm. partial pressure of the monomer, and this would have been demonstrated by the appearance of a fairly strong band near  $3600\text{ cm}^{-1}$ , expected for the free O-H stretching mode. The same band would have been expected if the dimer were based upon the formula  $\text{CF}_3\text{P}(\text{OH})_2$ , which seems to be eliminated by thermodynamic arguments as well.

The phosphinic-acid dimer structure is further supported by a strong band at  $1286\text{ cm}^{-1}$ , which seems assignable only to the  $\text{P}=\text{O}$  stretching mode, and by a medium-weak sharp peak at  $2425\text{ cm}^{-1}$ , perfectly characteristic of P-H stretching. As in other  $\text{CF}_3\text{-P-H}$  compounds, this P-H peak is accompanied by weaker satellites (at 2610, 2275, and  $2120\text{ cm}^{-1}$ ), representing overtones of  $\text{P}=\text{O}$  and C-F stretching modes, modified by Fermi resonance.

The C-F stretching modes are represented by a very strong peak at  $1228\text{ cm}^{-1}$  and an even stronger doublet at 1166 and  $1142\text{ cm}^{-1}$ . A very sharp peak at  $1307\text{ cm}^{-1}$  appearing in the middle of the side contour of the 1286 band might represent a combination including a mode beyond the range of the NaCl optics, or it might be due to a splitting of the  $\text{P}=\text{O}$  stretching mode by the molecular association.

Most of the remaining assignments are less certain, but at least there are no bands which cannot be explained. In the range expected for P-H bending we find a medium-intensity peak at  $999\text{ cm}^{-1}$  and a strong doublet at 955 and  $949\text{ cm}^{-1}$ , with a shoulder at  $945\text{ cm}^{-1}$ . These may include some bridge-framework vibrations. A weak, sharp peak at  $795\text{ cm}^{-1}$  probably represents P-O stretching, but the band contour might include a weaker band due to the asymmetric C-F bending mode (expected near  $765\text{ cm}^{-1}$ ), which is not otherwise in evidence.

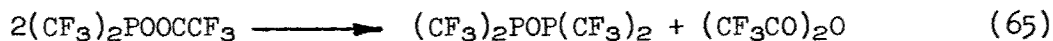


Our publication of all results concerning  $(\text{CF}_3\text{HPOOH})_2$  now has appeared in the Journal of the American Chemical Society.<sup>6</sup>

### B. Acetoxyposphines and their Consequences

Some four years ago W. Mahler (Ref. 7, page 28) attempted to make a  $(\text{CF}_3\text{PO})_n$  polymer by controlled action of oxygen upon the tetramer  $(\text{CF}_3\text{P})_4$ , but was able to obtain only  $(\text{CF}_3\text{PO}_2)_n$  polymers; no product corresponding to the half-way stage could be isolated. It was not possible to decide whether the desired  $\text{CF}_3\text{PO}$  material disproportionated too rapidly to be recognized or failed to form because the right mechanism was lacking; for example, since cold oxygen reactions normally begin with peroxide formation, the first step could be the formation of P-O-O bonds, followed by rapid conversion to the  $\text{P}=\text{O}$  situation. Thus a different approach was needed, and this was sought through the reactions of  $\text{CF}_3\text{-P-I}$  phosphines with silver trifluoroacetate, forming unstable acetoxyposphines which can dissociate with loss of the anhydride  $(\text{CF}_3\text{CO})_2\text{O}$  to form P-O-P bonds.

1. The Acetoxyposphine  $(\text{CF}_3)_2\text{POOCCF}_3$ . Before attempting the synthesis of the double acetoxyposphine  $\text{CF}_3\text{P}(\text{OCCF}_3)_2$  we considered it wise to learn something of the pertinent chemistry by studying first the simpler case of  $(\text{CF}_3)_2\text{POOCCF}_3$ . Accordingly, the synthesis of this compound was attempted by the reaction between  $\text{AgCO}_2\text{CF}_3$  and  $(\text{CF}_3)_2\text{PI}$ . In the initial experiment 1.59 mmoles of  $\text{AgCO}_2\text{CF}_3$  and 0.801 mmole of  $(\text{CF}_3)_2\text{PI}$  began to react at a fairly low temperature, showing the yellow color of  $\text{AgI}$ . Laborious fractionation yielded a very small sample of a volatile compound melting in the range  $-75.8$  to  $-75.3^\circ\text{C}$ . and with molecular weight 282; calcd. for  $(\text{CF}_3)_2\text{POOCCF}_3$ , 282.02. The reaction was repeated on a larger scale, using a series of fresh samples of  $\text{AgCO}_2\text{CF}_3$  to eliminate the last of the  $(\text{CF}_3)_2\text{PI}$ , but three techniques of fractionation failed to isolate the desired acetoxyposphine in pure form. It was evident that the product suffered disproportionation according to the equation



for the top fraction was virtually pure  $(\text{CF}_3\text{CO})_2\text{O}$  while the bottom fraction showed strong infrared bands characteristic of  $(\text{CF}_3)_2\text{POP}(\text{CF}_3)_2$  and had a molecular weight (310) considerably higher than that of pure  $(\text{CF}_3)_2\text{POOCCF}_3$ . Thus the expected loss of the perfluoro acetic anhydride and the formation of a P-O-P bond did indeed occur, with some possibility of control.

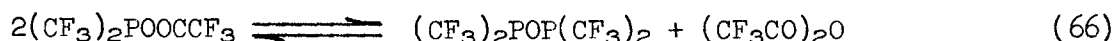
For the isolation of  $(\text{CF}_3)_2\text{POOCCF}_3$  the most nearly successful fractionation method employed a reflux column with the head at  $-65$  to  $-70^\circ\text{C}$ . (avoiding the solid-formation which occurred at  $-78^\circ\text{C}$ .) and with the effluent withdrawn through a finely adjusted stopcock into a high-vacuum trap. Thus eight middle-range fractions were obtained, having molecular weights ranging from 279 to 285 (calcd., 282) with vapor tensions from 59 to 57.5 mm. at  $0^\circ\text{C}$ .

The most representative middle fraction was used for a scan of the infrared spectrum for comparison with less pure samples and with the disproportionation products. Thus it was possible to make the following assignments specifically for the acetoxyposphine. C-F bending in the  $(\text{CF}_3)_2\text{P}$  group:  $730\text{mw}$  ( $\text{cm}^{-1}$ ). C-F bending in the C- $\text{CF}_3$  part:  $770\text{sh}$ . P-O stretching:  $785\text{m}$ . C-C stretching,  $855\text{w}$ . C-F stretching for two situations of the  $\text{CF}_3$  group:  $1104\text{s}$ ,  $1140\text{vs}$ ,  $1184\text{vs}$ ,  $1202\text{s}$ ,  $1229\text{s}$ , and  $1253\text{s}$ . C-O stretching:  $1343\text{ms}$  (higher than usual on account of electronegativity and some carboxyl resonance). C=O stretching:  $1818\text{s}$ . C-F stretching overtones and



and combinations: 2258vw, 2280vw, and 2418vww. C=O stretching overtone: 3590vww. The same scan showed bands belonging to the impurities: 670vww, 1058m, and 1883vw are known strong or very strong bands for the anhydride  $(\text{CF}_3\text{CO})_2\text{O}$ , while 925 is a known strong band for  $(\text{CF}_3)_2\text{POP}(\text{CF}_3)_2$ . Of the assignments for the acetoxypophosphine, only the four lowest-frequency bands may be regarded as somewhat uncertain or speculative.

The disproportionation of the acetoxypophosphine was shown to be reversible in an experiment wherein 0.481 mmole of  $(\text{CF}_3)_2\text{POP}(\text{CF}_3)_2$  and 1.532 mmoles of  $(\text{CF}_3\text{CO})_2\text{O}$  were left together in a sealed tube at room temperature for 64 hours. The mixture then showed infrared bands uniquely characteristic of the acetoxypophosphine, along with those of the original components. For the measurement of the equilibrium constant of the reaction



a mixture of  $(\text{CF}_3)_2\text{PI}$  and  $\text{AgCO}_2\text{CF}_3$  was brought to equilibrium and the product was sampled from the gas phase to give a known pressure within an infrared cell. The intensity of the  $1883\text{ cm}^{-1}$  band for the anhydride  $(\text{CF}_3\text{CO})_2\text{O}$  was compared with calibration values known for the pure substance; then it was possible to calculate, from the total pressure and the disproportionation equation, the partial pressures of the  $(\text{CF}_3)_2\text{POOCCF}_3$  and the  $(\text{CF}_3)_2\text{POP}(\text{CF}_3)_2$ .

The resulting equilibrium constant is defined in terms of the formation of the acetoxypophosphine:

$$K = \frac{[(\text{CF}_3)_2\text{POOCCF}_3]^2}{[(\text{CF}_3)_2\text{POP}(\text{CF}_3)_2][(\text{CF}_3\text{CO})_2\text{O}]} = \frac{(1.90)^2}{0.63 \times 0.63} = 9.1, \quad \text{for}$$

the case in which the total pressure was 3.16 mm. In a second experiment a 4.55 mm. partial pressure of the anhydride and 4.76 mm. of the diphosphoxane, equilibrated in the cell, went to 1.84 and 2.05 mm., respectively, giving K as 7.8. This value might be low, not only on account of a possible lack of perfect equilibration, but also because the higher pressure could have led to more interference by the strong  $1818\text{ cm}^{-1}$  band (present in the spectra of both the anhydride and the acetoxypophosphine) with the estimation of the intensity of the band at  $1883\text{ cm}^{-1}$ .

The rate of formation of the acetoxypophosphine was studied by observing the rate of decrease of intensity of the  $1883\text{ cm}^{-1}$  band in an equimolar mixture of the anhydride and the diphosphoxane. The decrease in the value of  $\log I_0/I$  for this band was initially rapid, but the rate became constant after 80 minutes at the standard chamber temperature ( $38^\circ\text{C}.$ ) of the IR7 instrument. At this point it seemed that the chief effect was absorption in the stopcock grease - a process which was still going on after 30 hours.

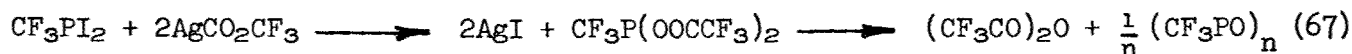
Our most recent synthesis of the acetoxypophosphine was done by passing a stream of  $(\text{CF}_3)_2\text{PI}$  vapor over a bed of  $\text{AgCO}_2\text{CF}_3$ . However, even under fairly fast flow conditions, the formation of the anhydride and the diphosphoxane amounted roughly to a 50% approach toward equilibrium. Since the acetoxypophosphine does not disproportionate so rapidly in storage as this result would suggest, it appears that the disproportionation is strongly promoted by the reaction conditions - whether by local heating or by a catalytic effect of the solid phase might be difficult to decide.

In sum, although the acetoxypophosphine could not be well characterized as a pure substance, its synthesis and study has encouraged an approach to  $(\text{CF}_3\text{PO})_n$



polymers through a similar study of  $\text{CF}_3\text{P}(\text{OOC}\text{CF}_3)_2$ .

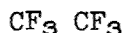
2. The Quest for  $(\text{CF}_3\text{PO})_n$  Polymers. A 492.7 mg. sample of  $\text{CF}_3\text{PI}_2$  with excess  $\text{AgCO}_2\text{CF}_3$  began to react on warming from a low temperature. After standing for ten hours at room temperature the mixture yielded 284.8 mg. of  $(\text{CF}_3\text{CO})_2\text{O}$ , or 97.5% of that expected in terms of the equation



The absence of  $(\text{CF}_3\text{P})_4$  and  $(\text{CF}_3\text{P})_5$  showed that the presumed  $\text{CF}_3\text{PO}$  polymer had not suffered the hypothetical disproportionation to form these and  $(\text{CF}_3\text{PO}_2)$  polymers. Also, the absence of  $\text{CO}_2$  and  $\text{CF}_3\text{I}$  excluded a conceivable side reaction in which the decomposition of the first-stage product  $\text{CF}_3\text{P}(\text{I})\text{OOC}\text{CF}_3$  would give  $\text{CF}_3\text{P}$  polymers,  $\text{CO}_2$ , and  $\text{CF}_3\text{I}$ .

After the removal of all material volatile at room temperature, the reaction tube was heated at  $100^\circ\text{C}$ . under high vacuum, evolving a further trace of  $(\text{CF}_3\text{CO})_2\text{O}$  and appreciable traces of other materials varying in volatility from 2 to 31 mm. at  $0^\circ\text{C}$ . Of these, the least volatile were noticeably unstable (with rising vapor tensions) and had complicated infrared spectra, including as many as four peaks in the  $\text{C}=\text{O}$  stretching region and three in the  $\text{C}-\text{O}$  stretching region. It appeared that some reaction might have occurred between the presumed  $(\text{CF}_3\text{PO})_n$  polymer and the  $\text{AgCO}_2\text{CF}_3$ . Much of the polymer remained in the form of a glassy film in the reaction tube, but there was some oily material which had distilled out. This was not appreciably volatile at room temperature.

The next experiment included a more definite attempt to isolate the diacetoxyposphine  $\text{CF}_3\text{P}(\text{OOC}\text{CF}_3)_2$ . A 1.5393 g. sample of  $\text{CF}_3\text{PI}_2$  was shaken for ten minutes with excess silver trifluoroacetate, yielding only 72% of the expected quantity of  $(\text{CF}_3\text{CO})_2\text{O}$ . The volatile product now included an unstable component which evolved  $(\text{CF}_3\text{CO})_2\text{O}$  during attempts to isolate it by fractionation. The fraction which seemed to be richest in this component had a vapor tension of 6.0 mm. at  $0^\circ\text{C}$ . (same after refractionation) and an average molecular weight of 332 (calcd. for the diacetoxyposphine, 326.0). The infrared spectrum also indicated a major proportion of the desired diacetoxyposphine: two kinds of  $\text{CF}_3$  groups with  $\text{C}-\text{F}$  bending at wave numbers 728m and 775 sh (with 759m unassigned) and  $\text{C}-\text{F}$  stretching at 1075, 1125, 1166, 1203, 1224, and 1253 (all very intense);  $\text{P}-\text{O}$  stretching at 800m;  $\text{C}-\text{C}$  stretching at 850m;  $\text{C}-\text{O}$  stretching at 1349ms;  $\text{C}=\text{O}$  stretching at 1828s with an overtone at 3600w. Bands at 912 and 988 (both weak) probably are due to  $\text{P}-\text{O}-\text{P}$  stretching in some such impurity as  $\text{CF}_3\text{COOP}-\text{O}-\text{POOC}\text{CF}_3$ . This would represent an intermediate



stage in the conversion of the diacetoxyposphine to  $\text{CF}_3\text{PO}$  polymers and  $(\text{CF}_3\text{CO})_2\text{O}$ , and would account for the previously-observed unstable bottom fractions. It would also explain molecular weights ranging from 332 to 392 for these fractions. The least volatile fraction (2.0 mm. at  $0^\circ\text{C}$ .) absorbed at  $920 \text{ cm}^{-1}$ , demonstrating  $\text{P}-\text{O}-\text{P}$  stretching. It was allowed to stand for eight weeks at room temperature, condensing to crystalline solids and other nonvolatile material of more plastic character.



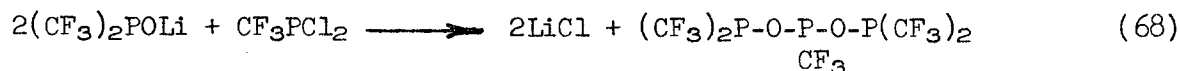
The nonvolatile polymer, remaining in the reaction tube with the excess  $\text{AgCO}_2\text{CF}_3$  and the  $\text{AgI}$  formed in this second experiment, was extracted by toluene, in which it proved to be readily soluble. However, some of the  $\text{AgCO}_2\text{CF}_3$  also dissolved, making it difficult to isolate the polymer by low-temperature crystallization techniques; the fine crystals included the silver salt. The toluene was removed by evaporation in vacuo, and the residue was heated to remove any sublimable component; however, the polymer only became waxy and melted at  $90^\circ\text{C}$ . to a viscous liquid, evolving no vapor at all. Placed between two  $\text{NaCl}$  windows, it absorbed at  $920\text{ cm}^{-1}$  (asymmetric P-O-P stretching) and also showed the C=O stretching mode which could be ascribed to  $\text{AgCO}_2\text{CF}_3$  as well as to an acetoxy group on P.

It appeared that the extracting solvent, toluene, might have suffered some change, for it now contained a difficultly separable component with molecular weight values determined as 160 and 185, and having an infrared spectrum indicating C-H material, as well as C-O, C=O, and C-F bonds. A different solvent is required, but the polymer proved insoluble in hexane.

Further attempts to isolate the  $(\text{CF}_3\text{PO})_n$  polymer included a heating with excess  $(\text{CF}_3\text{CO})_2\text{O}$ , which might have been expected to convert it partially to volatile acetoxyposphines capable of condensation back to the polymer by release of  $(\text{CF}_3\text{CO})_2\text{O}$ . However, there was very little reaction; such volatile product as could be observed contained C-H material, possibly to be ascribed to stop-cock grease. Doubtless it will be possible to find a solvent other than toluene, for extracting the polymer from the silver salts, but another possibility worth considering would be base-depolymerization to a monomer-complex such as  $(\text{CH}_3)_3\text{P}\cdot\text{CF}_3\text{PO}$ , which might be expected to be at least as stable as the known monomer-complex  $(\text{CH}_3)_3\text{P}\cdot\text{PCF}_3$  (see Section III.).

#### C. Other Approaches Toward $(\text{CF}_3\text{PO})_n$ Polymers

It was conceived that the reaction



would offer a useful approach to the  $\text{CF}_3\text{PO}$  polymers, for the resulting triphosphi-dioxane would represent the desired type of polymer bonding in the simplest possible way, and also might be expected to decompose into  $(\text{CF}_3)_2\text{POP}(\text{CF}_3)_2$  and  $\text{CF}_3\text{PO}$  units on standing, thus providing a direct method of forming  $(\text{CF}_3\text{PO})_n$  polymers. Accordingly, a sample of  $(\text{CF}_3)_2\text{POH}$  was put to reaction with  $\text{LiC}_4\text{H}_9$  in hexane (with slow warming to  $-40^\circ\text{C}$ .), producing more than half of the expected butane and a white precipitate presumed to be  $(\text{CF}_3)_2\text{POLi}$ . However, the reaction of this product with  $(\text{CF}_3)_2\text{PCl}$  did not lead to the isolation of  $(\text{CF}_3)_2\text{POP}(\text{CF}_3)_2$  as expected. The infrared spectrum did show some P-O-P bonding (band at  $920\text{ cm}^{-1}$ ) but C-H stretching frequencies showed the presence also of some hydrocarbon material. Thus we shall not attempt to use the lithium salt for the more complex synthesis of the desired triphosphi-dioxane; rather it seems better



to try a bubbling of  $(\text{CH}_3)_3\text{N}$  into a low-temperature solution of  $(\text{CF}_3)_2\text{POH}$  and  $\text{CF}_3\text{PCl}_2$ . Thus the destructive basic action can be avoided, as the salt  $(\text{CF}_3)_2\text{POMe}_3\text{NH}$  will be formed just as it is used by the reaction.

Our original method of making  $(\text{CF}_3)_2\text{POH}$ , by the action of  $\text{HCl}$  upon  $(\text{CF}_3)_2\text{POP}(\text{CF}_3)_2$ , utilized only half of the  $(\text{CF}_3)_2\text{P}$  groups. In the hope of a more efficient process, we have made the ester  $(\text{CF}_3)_2\text{POCH}_3$  from  $(\text{CF}_3)_2\text{PCl}$  and  $\text{CH}_3\text{OH}$  (just as Emeléus and Smith had made the ethyl ester),<sup>8</sup> and treated it with  $\text{HBr}$ . The intent was a reaction parallel to the conversion of  $\text{CF}_3\text{P}(\text{OCH}_3)_2$  to  $(\text{CF}_3\text{PHOOH})_2$  and  $\text{CH}_3\text{Br}$  by action of  $\text{HBr}$ .<sup>6</sup> However this time there were side reactions:  $\text{CH}_3\text{Br}$  appeared, but also unknown phosphine oxides were indicated by the infrared spectra of some less volatile fractions. The process is not effective for  $(\text{CF}_3)_2\text{POH}$ .

1. Other Possible Oxy-Polyphosphines. Our new polyphosphine syntheses (see Section III, near end) encountered an impurity which probably was a ring oxy-polyphosphine, a more direct synthesis of which would be interesting.

#### D. Physical Characterization of Reagents

For the work on oxyphosphines it was important to employ pure samples of such reagents as  $(\text{CF}_3)_2\text{PI}$ ,  $(\text{CF}_3)_2\text{PCl}$ , and  $\text{CF}_3\text{PCl}_2$ . In general, it is well to be able to check the purity of these materials, which are used for numerous other syntheses of trifluoromethylphosphines, but the requisite knowledge of their physical properties has been lacking. This need now is met.

1. Bis(trifluoromethyl)iodophosphine. Samples of  $(\text{CF}_3)_2\text{PI}$  from the  $\text{AgCO}_2\text{CF}_3\text{-P}_X\text{-I}_2$  process usually contain oxyphosphine impurities; and samples from any source probably have some  $\text{P}_2(\text{CF}_3)_4$ , resulting from spontaneous loss of iodine. Hence for a pure sample of  $(\text{CF}_3)_2\text{PI}$  we purified a sample of  $\text{P}_2(\text{CF}_3)_4$  by shaking it with water for extended periods of time, drying it by calcium sulfate, and fractionating it under reflux; then this sample was treated with iodine in excess and the resulting  $(\text{CF}_3)_2\text{PI}$  was purified by reflux fractionation until its vapor tension at  $0^\circ\text{C}$ . was constant. The vapor tensions of this product were obtained by means of a sensitive spoon-gauge serving as a null instrument. The results are shown with an equation in Table XXII, indicating the normal b.p. as  $70.9^\circ\text{C}$ ., the enthalpy of vaporization as 7257 cal./mole, and the Trouton constant as 21.1 cal./deg. mole.

TABLE XXII

#### Vapor Tensions of Liquid $(\text{CF}_3)_2\text{PI}$

$$(\log P_{\text{mm}} = 5.9341 + 1.75 \log T - 0.005286T - 1952/T)$$

t ( $^\circ\text{C}$ .)	0.00	15.6	25.4	32.7	41.5	47.4	38.1	26.75
$P_{\text{mm}}$ (obsd.)	40.5	90.1	141.0	192.5	275.1	343.6	238.8	151.0
$P_{\text{mm}}$ (calcd.)	40.5	89.9	140.9	192.8	274.5	343.2	240.2	149.6



The last two points of this table represent readings taken after cooling from the highest temperature of measurement, showing that decomposition did not affect the results.

The infrared spectrum of  $(\text{CF}_3)_2\text{PI}$  is shown in Table XXV.

2. Bis(trifluoromethyl)chlorophosphine. Pure  $(\text{CF}_3)_2\text{PI}$  was allowed to react with pure, dry  $\text{HgCl}_2$  in excess and the resulting  $(\text{CF}_3)_2\text{PCl}$  was column-fractionated (with reflux at  $-96^\circ\text{C}.$ ) until its vapor tension at  $-22.70^\circ\text{C}.$  was constant. The vapor tension values (mercury manometer, corrected) are shown with an equation in Table XXIII. The normal b.p. is calculated as  $23.1^\circ\text{C}.$ , the molar enthalpy of vaporization as 6536 cal., and the Trouton constant as 22.06 cal./deg. mole.

TABLE XXIII

Vapor Tensions of Liquid  $(\text{CF}_3)_2\text{PCl}$

$$(\log P_{\text{mm}} = 4.1457 + 1.75 \log T - 0.002582T - 1429/T)$$

t ( $^\circ\text{C}.$ )	-80.8	-64.8	-46.00	-31.40	-22.70	0.00
$P_{\text{mm}}$ (obsd.)	1.65	6.38	24.96	60.11	98.06	297.0
$P_{\text{mm}}$ (calcd.)	1.65	6.42	24.66	60.49	98.02	297.0

The infrared spectrum of  $(\text{CF}_3)_2\text{PCl}$  is shown in Table XXV.

3. Trifluoromethyl-dichlorophosphine. A sample of  $\text{CF}_3\text{PI}_2$  was purified by high-vacuum fractionation and brought to reaction with  $\text{HgCl}_2$  in excess. The resulting  $\text{CF}_3\text{PCl}_2$  was fractionated until its vapor tension at  $0^\circ\text{C}.$  was constant for six fractions. Then a middle fraction was used for vapor tension measurements, employing a mercury manometer. The results, shown with an equation in Table XXIV, indicate the normal b.p. as  $39.3^\circ\text{C}.$ , the molar enthalpy of vaporization as 6800 cal., and the Trouton constant as 21.76 cal./deg. mole.

TABLE XXIV

Vapor Tensions of Liquid  $\text{CF}_3\text{PCl}_2$

$$(\log P_{\text{mm}} = 4.22534 + 1.75 \log T - 0.0027426T - 1516/T)$$

t ( $^\circ\text{C}.$ )	-64.75	-46.00	-27.10	-11.35	0.00	10.15	17.30
$P_{\text{mm}}$ (obsd.)	2.74	11.36	36.9	89.9	154.9	244.8	331.0
$P_{\text{mm}}$ (calcd.)	2.74	11.28	37.5	88.8	154.9	244.8	331.0



The melting points of two different fractions of  $\text{CF}_3\text{PCl}_2$  were measured as  $-129.4$  and  $-129.6^\circ\text{C}.$ , using the Stock plunger type of melting point apparatus with an ethylene vapor-tension thermometer. The infrared absorption frequencies are given in Table XXV.

4. Infrared Spectra. The frequencies shown in Table XXV were obtained from spectra recorded by the Beckman IR7 instrument, at low pressures for accurate observation of very intense bands and at higher pressures to detect very weak bands. The symbols for intensity have the same meaning as in Table XXI; and in some cases the symbol b is used to indicate a relative broad band with an uncertain peak, and sh to indicate a shoulder. Where no assignment is suggested, the band is presumed to represent an overtone or combination; however most of these are difficult to relate to the fundamentals.



TABLE XXV

Infrared Absorption Frequencies  
of Three  $\text{CF}_3$ -halo-phosphines(Frequencies in  $\text{cm}^{-1}$ )

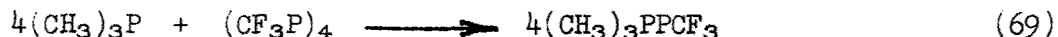
Probable Assignment	$(\text{CF}_3)_2\text{PI}$	$(\text{CF}_3)_2\text{PCl}$	$\text{CF}_3\text{PCl}_2$
(Overtones and Combinations)	2274 wb 2234 w 1950 vw 1903 w 1864 w 1375 wb 1259 mw	2425 w 2350 mw 2288 mw 2250 mw 1992 ww 1959 ww 1912 vw 1878 vw 1400 w 1303 mw 1297 mw 1275 m 1266 m	2388 w 2313 w 2288 mw 1994 ww 1941 w 1892 w 1306 sh 1299 m 1292 m 1281 m 1275 m 1269 m
C-F stretching	1189 s 1166 vss 1136 ss 1122 vs	1219 ss 1178 ss 1135 ss	1202 ss 1173 sh 1156 ss 1122 sh
(Overtones and Combinations)	1091 m 1026 w 984 wb	1028 ww  894 ww 859 ww	1077 sh 1047 vw 994 vw 950 vw 900 vw 854 vw
Asymmetric C-P-C stretch; C-F bending	751 ms 749 ms 747 ms	756 m 749 m 746 m	753 m 745 m
(Uncertain)	719 w	725 w	725 w 719 w 675 vw 667 vw



### III. Trifluoromethyl-Polyphosphines

#### A. Basic Depolymerization of $(\text{CF}_3\text{P})_n$ Rings

The reaction indicated in equation 69 was reported from our laboratories some time ago (Ref. 9, page 95), but there remained some uncertainties as to its extent of completion under various conditions.



Recent studies on this subject, taken with results reported to us by our former colleague Walter Mahler (now with the duPont Co. in Wilmington, Delaware) show quite clearly that the reaction is less than 90% complete in solution, even when the solvent is trimethylphosphine; but when the solid monomer-adduct is formed by the action of the tertiary-phosphine vapor upon solid  $(\text{CF}_3\text{P})_4$ , the reaction comes very close to completion. The reason for this difference must be found in the energy difference between the solid and the solution. In solution there is no solid-state energy to favor the complex, so that it is possible to establish a state of equilibrium short of complete depolymerization of the  $(\text{CF}_3\text{P})_4$ . In the solid-state reaction, however, there are three phases present (gas and two solids) while the phosphine is being absorbed; hence the pressure must remain constant at any fixed temperature, until the  $(\text{CF}_3\text{P})_4$  solid phase has been entirely converted to  $(\text{CH}_3)_3\text{PPCF}_3$ .

Our first evidence of incomplete reaction in solution came from determination of the molecular weight: the results all ran at least 25% high even at  $\text{CF}_3\text{P}$  concentrations as low as 0.7 mole percent, but did not exceed 40% high even at much higher concentrations. Furthermore, the trimethylphosphine solutions could be chilled to  $-78^\circ\text{C}$ . and freed of excess  $(\text{CH}_3)_3\text{P}$  by slow distillation in vacuo at that temperature, and then it is found that no more than  $0.88(\text{CH}_3)_3\text{P}$  per  $\text{CF}_3\text{P}$  unit has remained in combination. Since the 1:1 complex has been found to be entirely stable under high vacuum at  $-45^\circ\text{C}$ ., this result can only mean that it was incompletely formed in the solution in spite of the great excess of trimethylphosphine. Further confirmation has come from the nuclear magnetic resonance spectra reported to us by Dr. Mahler: lines quite characteristic of  $(\text{CF}_3\text{P})_4$  and  $(\text{CF}_3\text{P})_5$  were found in minor intensity in various solutions of the monomer-complex.

The gas-solid reaction for the formation of the monomer-complex was studied by observing the constant 12 mm. pressure at  $23^\circ\text{C}$ . as the  $(\text{CH}_3)_3\text{P}$  content of the solid went from zero to  $0.98(\text{CH}_3)_3\text{P}$  per  $\text{CF}_3\text{P}$  unit. In mid-range of the addition, the pressure at  $43^\circ\text{C}$ . was measured as 53 mm. The two pressures and temperatures determined the equation  $\log P_{\text{mm}} = 11.276 - 3020/T$  (calcd. for  $0^\circ\text{C}$ ., 1.69 mm.; obsd., 1.65). Defining the equilibrium constant  $K$  as the dissociation pressure in atmospheres, this means that  $\Delta F^\circ = 13.82 - 0.0384T$  kcal. for the dissociation of one mole of  $(\text{CH}_3)_3\text{PPCF}_3$  to  $(\text{CH}_3)_3\text{P}$  and  $(\text{CF}_3\text{P})_4$ . As before, complete dissociation could be accomplished by high-vacuum fractional condensation, with all of the trimethylphosphine passing a trap at  $-78^\circ\text{C}$ .



Another item of information from Dr. Mahler was his observation that the ratio of  $(\text{CF}_3\text{P})_5$  to  $(\text{CF}_3\text{P})_4$  in solution in a tertiary base is considerably higher than when these ring compounds are in equilibrium in the presence of a catalytic trace of a tertiary base. The reason presumably is again the loss of solid-state stabilization when the tetramer is put into solution, whereas the pentamer is a liquid anyway. Thus by working in solution and allowing adequate time for equilibrium to be established, it is quite feasible to convert  $(\text{CF}_3\text{P})_4$  to  $(\text{CF}_3\text{P})_5$  in practical yields.

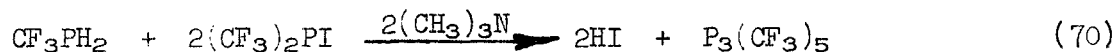
All of our present knowledge of such base- $\text{PCF}_3$  complexes now has been published--including the duPont work on the NMR spectra, showing agreement with the structural pattern implied by the formula  $(\text{CH}_3)_3\text{PPCF}_3$ .<sup>10</sup>

## B. The New Triphosphine $\text{P}_3(\text{CF}_3)_5$

Control of the  $\text{CF}_3\text{P}$  unit for chemical purposes is desirable and is accomplished only with some limitations, by the use of the monomer-complex  $(\text{CH}_3)_3\text{PPCF}_3$ . Another approach might be found in the use of an unstable open-chain polyphosphine, for it is known that the triphosphine  $\text{H}_2(\text{CF}_3\text{P})_3$  decomposes to form  $(\text{CF}_3\text{PH})_2$  and  $\text{CF}_3\text{P}$  polymers (Ref. 9, page 29), so that the  $\text{CF}_3\text{P}$  unit should be available in a fairly reactive form during the decomposition. For many purposes, however, it will be important to avoid the P-H bond, so that a triphosphine such as  $\text{P}_3(\text{CF}_3)_5$  might be a better source of the  $\text{CF}_3\text{P}$  unit with minimal side reactions. Accordingly, we have learned to make this new triphosphine in good yields, and have made a preliminary study of its chemical character.

### 1. Initial Synthesis

The first successful process for the synthesis of  $\text{P}_3(\text{CF}_3)_5$  was the phosphinolysis indicated in equation 70.



For this purpose,  $\text{CF}_3\text{PH}_2$  was made in 88% yield by the vigorous action of  $\text{PH}_3$  upon 0.45 as many millimoles of  $\text{CF}_3\text{PI}_2$ , in a sealed tube warming to room temperature. The identity of the product was confirmed by its characteristic infrared spectrum as well as the molecular weight (101 vs. calcd. 102) and vapor tension at  $-78.5^\circ\text{C}$ . (45.0 mm.).

The initial experiment was directed toward the synthesis of an intermediate biphosphine,  $(\text{CF}_3)_2\text{PPHCF}_3$ , and accordingly employed equimolar proportions of  $\text{CF}_3\text{PH}_2$ ,  $(\text{CF}_3)_2\text{PI}$ , and  $(\text{CH}_3)_3\text{N}$ . However, the sealed-tube reaction at  $-78^\circ\text{C}$ . (overnight) seemed mostly to skip past the intermediate, only a small yield of which was indicated by a P-H bending frequency ( $1080\text{ cm}^{-1}$ ) in the infrared spectrum of a fraction (41 mm. at  $0^\circ\text{C}$ .) containing a high proportion of the known biphosphine  $\text{P}_2(\text{CF}_3)_4$ . The larger fraction (liquid at  $-45^\circ\text{C}$ .) had properties which, taken with later information, indicated a mixture of  $\text{CF}_3\text{P}$  polymers and the new  $\text{P}_3(\text{CF}_3)_5$ . Just half of the initial sample of  $\text{CF}_3\text{PH}_2$  was recovered



and identified. The triphosphine proved to be difficult to deal with, for Apiezon L stop-cock grease caused decomposition, and even mercury seemed to be mildly catalytic.

In a second experiment of the same kind, but on a larger scale, the reaction began immediately at  $-78^{\circ}\text{C}$ . (as shown by the formation of a white solid) but was not completed even during the overnight period, for the mixture of volatiles reacted further after removal to other parts of the high-vacuum system. Presumably the solid trapped some of the reactants, which then were brought forth by the high-vacuum distillation at higher temperatures. In this case halocarbon stop-cock grease was used, and it was possible to estimate the yield of  $\text{P}_3(\text{CF}_3)_5$  as near 30%, based upon the initial sample of  $(\text{CF}_3)_2\text{PI}$ . The recovery of unused  $\text{CF}_3\text{PH}_2$  amounted to 35%.

The third experiment employed 2.264 mmoles of  $(\text{CF}_3)_2\text{PI}$ , 1.144 mmoles of  $\text{CF}_3\text{PH}_2$  and 2.323 mmoles of  $(\text{CH}_3)_3\text{N}$ , roughly in conformity to the initial plan for  $\text{P}_3(\text{CF}_3)_5$ . The reaction again was not quite complete even after three weeks at  $-78^{\circ}\text{C}$ ., but was finished by distilling the volatile components back and forth between high-vacuum traps until no more solid was formed. Thus the original reactants were eliminated, except for the recovery of 0.008 mmole of  $\text{CF}_3\text{PH}_2$ . The yield of  $\text{P}_3(\text{CF}_3)_5$  again amounted to barely 30% of the  $(\text{CF}_3)_2\text{PI}$ , and the yield of the biphosphine  $\text{P}_2(\text{CF}_3)_4$  was actually higher--0.435 mmole, or 38%. A fraction purporting to be the intermediate biphosphine  $(\text{CF}_3)_2\text{PPHCF}_3$  (mol. wt. 269.6 vs. calcd. 270.0; vapor tension 61.3 mm. at  $0^{\circ}\text{C}$ .) amounted to 60.1 mg., or 0.225 mmole. Its infrared spectrum did not distinctly show the P-H stretching mode near  $2270\text{ cm}^{-1}$  (where the C-F stretching overtones could have interfered), but the medium-strong band at  $1070\text{ cm}^{-1}$  may well represent the P-H bending mode. The compound seemed to be unstable, for repeated distillations for purification gave small fractions of  $(\text{CF}_3)_2\text{PH}$  and  $\text{CF}_3\text{P}$ -ring polymers.

The relatively high yields of  $\text{P}_2(\text{CF}_3)_4$  might have three sources: (1) removal of iodine from  $(\text{CF}_3)_2\text{PI}$  by the amine; (2) the presence of this biphosphine as a large impurity in the original sample of  $(\text{CF}_3)_2\text{PI}$ ; and (3) decomposition of the triphosphine  $\text{P}_3(\text{CF}_3)_5$  to  $\text{P}_2(\text{CF}_3)_4$  and  $\text{CF}_3\text{P}$  polymers. The first of these seems improbable in view of the low temperature of the experiment, but the second proved to be quite real. It seems that even the original synthesis of the  $\text{CF}_3\text{-P-I}$  compounds, from phosphorus, iodine, and  $\text{CF}_3\text{I}$ , probably gives some  $\text{P}_2(\text{CF}_3)_4$  which is not easily noticed because its volatility is not far from that of  $(\text{CF}_3)_2\text{PI}$ . Or, if a pure sample of  $(\text{CF}_3)_2\text{PI}$  is allowed to stand for some time at room temperature, it forms a trace of iodine which normally is left behind when the sample is distilled out for use in a reaction; however, the corresponding trace of  $\text{P}_2(\text{CF}_3)_4$  remains with the sample. But the third source of  $\text{P}_2(\text{CF}_3)_4$  probably is the most important, for trimethylamine would be expected to catalyze the process, just as tertiary bases are known to catalyze the decomposition of  $\text{H}_2(\text{CF}_3\text{P})_3$  or the equilibration of the  $\text{CF}_3\text{P}$  tetramer-pentamer mixtures. The importance of this catalyzed decomposition of  $\text{P}_3(\text{CF}_3)_5$  seems to be demonstrated by the results of an experiment using pure  $(\text{CF}_3)_2\text{PCl}$  instead of  $(\text{CF}_3)_2\text{PI}$ , as next described.



## 2. The $(\text{CF}_3)_2\text{PCl}-\text{CF}_3\text{PH}_2-(\text{CH}_3)_3\text{N}$ Reaction

Pure  $(\text{CF}_3)_2\text{PCl}$  was made by a new method, using  $(\text{CF}_3)_2\text{PI}$  with  $\text{HgCl}_2$  instead of  $\text{AgCl}$ . The immediate formation of the red mercuric iodide signalled a considerably faster reaction than occurs with  $\text{AgCl}$ . Then a 1.061 mmole sample of  $(\text{CF}_3)_2\text{PCl}$ , with 0.562 mmole of  $\text{CF}_3\text{PH}_2$  and 1.091 mmoles of  $(\text{CH}_3)_3\text{N}$ , reacted rapidly at  $-78^\circ\text{C}$ ., once again incompletely so that the process had to be finished by trap-to-trap distillation as before. The products included 0.153 mmole of  $\text{P}_3(\text{CF}_3)_5$  (29% yield), 0.271 mmole of  $\text{P}_2(\text{CF}_3)_4$  (51% yield), and unmeasured amounts of  $(\text{CF}_3\text{P})_4$  and  $(\text{CF}_3\text{P})_5$ . Since  $\text{P}_2(\text{CF}_3)_4$  sources (1) and (2) would not apply to this situation, it seems that the large yield of  $\text{P}_2(\text{CF}_3)_4$  could only have been due to the amine-catalyzed decomposition of the  $\text{P}_3(\text{CF}_3)_5$ --the yield of which was virtually the same as from  $(\text{CF}_3)_2\text{PI}$ .

## 3. The Synthesis in Solution

It was considered that the  $(\text{CF}_3)_2\text{PI}-\text{CF}_3\text{PH}_2-(\text{CH}_3)_3\text{N}$  reaction might produce  $\text{P}_3(\text{CF}_3)_5$  more efficiently if done in solution, so that mixing could be more effective and local heating effects could be avoided. The chosen solvent was n-pentane, which was purified by the action of bromine to destroy any unsaturation, followed by drying in contact with calcium hydride, and fractional distillation to uniformity. Having a vapor tension near 1 mm. at  $-78^\circ\text{C}$ ., this solvent would not seriously interfere with the isolation of the pertinent components of the reaction mixture.

The reaction was carried out in a U-tube with about 5 ml. bulb-capacity below the bend, and fitted with two side arms (one on each shoulder) serving as condensation points for the most volatile reactant,  $\text{CF}_3\text{PH}_2$ . This apparatus was attached to the high-vacuum system through a ground joint and stop-cock. The  $(\text{CF}_3)_2\text{PI}$  (5.919 mmoles) was dissolved in just enough pentane to bring the level of the yellowish solution above the bend of the U-tube at  $-78^\circ\text{C}$ .. Next the trimethylamine (5.150 mmoles) was introduced, forming a white solid which doubtless was the expected 1:1 adduct. This evidently was not stable enough to interfere with the desired reaction, for it disappeared on slight warming, and then some of the amine could be distilled off.

Now small portions of  $\text{CF}_3\text{PH}_2$  were successively brought in by condensation into the side-arm nearest to the high-vacuum system, and bubbled back and forth from one side-arm to the other, through the solution at  $-78^\circ\text{C}$ . until all absorbed (two or three passes usually sufficed). Thus the introduction of 2.624 mmoles of  $\text{CF}_3\text{PH}_2$  went on during 1.5 hours, after which the reaction mixture was left for a further two hours at  $-78^\circ\text{C}$ .. As in the experiments without a solvent, the reaction was indicated by rapid formation of a white precipitate; yet some further reaction was observed afterwards when the volatiles were distilled back and forth in the high-vacuum system. In order best to conserve the desired product, this was isolated before the over-all reaction was quite complete, and the more volatile solvent and reactants were distilled to new tubes until no further reaction was apparent.

This experiment yielded 1.125 mmoles of  $\text{P}_3(\text{CF}_3)_5$ , and the recovery of  $\text{CF}_3\text{PH}_2$  was 0.086 mmole. The percent yield of the triphosphine is based upon



the consumed  $\text{CF}_3\text{PH}_2$  because the  $(\text{CF}_3)_2\text{PI}$  was somewhat in excess. The result, 44.3%, indicates some improvement over the experiments without a solvent, but it appears that far more improvement might be possible if some control of the catalytic effect of the amine could be achieved. A least measure of the importance of this effect is provided by the yield of polymeric  $\text{CF}_3\text{P}$  units--0.342 mmole. The corresponding  $\text{P}_2(\text{CF}_3)_4$  and the unused  $(\text{CF}_3)_2\text{PI}$  were not isolated.

#### 4. Characterization

The triphosphine  $\text{P}_3(\text{CF}_3)_5$  was purified by exhaustive fractional condensation. It was not too hard to remove the less volatile  $(\text{CF}_3\text{P})_4$  and  $(\text{CF}_3\text{P})_5$  by passing the sample slowly through a trap at  $-35^\circ\text{C}$ ., but the elimination of the considerably more volatile  $\text{P}_2(\text{CF}_3)_4$  through traps at lower temperatures actually proved to be more difficult. It was necessary to avoid any contact with Apiezon L grease, but halocarbon grease could be used in the stopcocks, and a mercury float-valve system could be employed without any noticeable decomposition during fairly short periods of contact at room temperature.

The molecular weight determinations were done by volume measurement in an immersible tensimeter at 35, 43, and  $51^\circ\text{C}$ ., with no difficulty from the manometer mercury when the immersion was done suddenly and the reading taken quickly. The results were 437.9, 441.0, and 443.0; calcd., 438.0.

The vapor-tension measurements above room temperature also had to be done quickly, by immersing the tensimeter suddenly in the warm bath, observing quickly, and recooling the tensimeter. The sample was rechecked at a lower temperature after each such measurement, and repurified if necessary. Even so, the results, shown in Table XXVI indicate an unusually high Trouton constant, not to be explained easily on the basis of high purity. This value, 26.0 cal./deg.-mole, corresponds to the calculated b.p.  $130.4^\circ\text{C}$ ., which probably is too low. An attempt to fit a Nernst-type three-parameter equation to the same data led to the b.p.  $132.5^\circ\text{C}$ . and Trouton constant 25.4. The deviation from normal behavior probably is to be explained in terms of unavoidable traces of the more volatile decomposition product,  $\text{P}_2(\text{CF}_3)_4$ .

TABLE XXVI

#### Vapor Tensions of Liquid $\text{P}_3(\text{CF}_3)_5$

$$(\log_{10}P_{\text{mm}} = 8.5600 - 2292/T)$$

t ( $^\circ\text{C}$ .)	0.00	8.4	15.9	23.9	46.1	60.1
$P_{\text{mm}}$ (obsd.)	1.51	2.63	4.25	7.01	24.2	47.8
$P_{\text{mm}}$ (calcd.)	1.48	2.63	4.28	6.99	24.0	48.1



The ultraviolet spectrum of  $P_3(CF_3)_5$  showed a strong maximum at 2210 Å., characteristic of the electronic delocalization associated with P-P bonding in polyphosphines. The infrared spectrum showed only peaks characteristic of P-CF<sub>3</sub> bonding, including the C-F stretching multiplicity of (CF<sub>3</sub>)<sub>2</sub>P groups.

#### 5. Proof of Formula

The formula  $P_3(CF_3)_5$  was proved by quantitative conversion to other known polyphosphines. In the first experiment, the 29.0 mg. sample had a brief contact with Apiezon L grease, introducing P-H bonds. Thus after 18 hours at 120°C. the sample yielded 3.8 mg. of (CF<sub>3</sub>)<sub>2</sub>PH, along with 6.5 mg. of CF<sub>3</sub>P polymers and 18.5 mg. of  $P_2(CF_3)_4$ . This result means that a 0.0662 mmole sample of  $P_3(CF_3)_5$  contained 0.065 mmole of CF<sub>3</sub>P units and 0.132 mmole of (CF<sub>3</sub>)<sub>2</sub>P units (calcd., 0.066 and 0.132). In a second experiment, a 50.5 mg. sample (carefully guarded against grease effects) was heated in a sealed tube for 6 hours at 110°C. but was not all decomposed in that time — evidently being stabler under these conditions than when the vapor tensions were measured in the glass-mercury system. After a briefer heating to 170°C. however, there was no more triphosphine. The products were 11.5 mg. of (CF<sub>3</sub>P)<sub>4</sub>, 30.3 mg. of  $P_2(CF_3)_4$ , 5.8 mg. of (CF<sub>3</sub>)<sub>3</sub>P, and 2.9 mg. of a brown non-volatile material. The last two would correspond to the thermal decomposition of 0.025 mmole of  $P_2(CF_3)_4$ , the total of which is indicated as 0.114 mmole (calcd., 0.115). The (CF<sub>3</sub>P)<sub>4</sub> amounted to 0.115 mmole of CF<sub>3</sub>P units (calcd., 0.115). These results, taken with the molecular weight determinations, leave no doubt of the formula  $P_3(CF_3)_5$ .

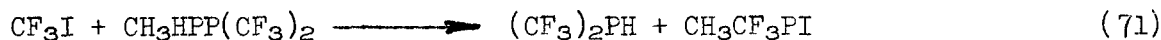
#### C. Polyphosphine Approaches to CH<sub>3</sub>CF<sub>3</sub>P-Compounds

Our erstwhile colleague Dr. K. K. Joshi had explored a number of approaches toward the chemistry of compounds of the CH<sub>3</sub>CF<sub>3</sub>P unit (Ref. 2, pp. 174-80), with the purpose of finding a relatively expeditious method for the large-scale synthesis of such compounds. This effort seemed important because the very different chemistry of alkyl versus perfluoro-alkyl phosphines implied a state of complete uncertainty concerning much of the chemistry of compounds representing the mean between those extremes. Furthermore, there is an attractive possibility that the intermediate chemistry will prove more useful for polymer purposes than either extreme; for example, when phosphorus holds only one CF<sub>3</sub> group, it is more difficult to remove it than to take off one of two CF<sub>3</sub> groups on P. Or, to consider another example, if one uses the biphosphine (CH<sub>3</sub>CF<sub>3</sub>P)<sub>2</sub> to make an ethylene-connected diphosphine, this could be used to make a C-P-B-H resin which should lose HCF<sub>3</sub> during extreme heating, with an automatic increase in the bonding of phosphorus to the boron-hydride polymer component.

We now have rechecked some of Dr. Joshi's methods of synthesis of CH<sub>3</sub>CF<sub>3</sub>PI, arriving at an improved basis for choice of the best way forward.

##### 1. The Biphosphine Process

Dr. Joshi had performed a single experiment indicating a fairly satisfactory yield of CH<sub>3</sub>CF<sub>3</sub>PI from the reaction (Ref. 2, p. 188);





but after the submission of our Annual Report including that item, he tried in vain to repeat the conditions leading to any yield at all, of the desired phosphine. We now have tried simple mixtures of the reactants under the following conditions, obtaining no yield of  $\text{CH}_3\text{CF}_3\text{PI}$ :

- (1) Standing in a sealed tube for five days at  $25^\circ\text{C}$ .;
- (2) Room-temperature irradiation by sunlight or a mercury arc;
- (3) Heating at  $75^\circ\text{C}$ . for five hours;
- (4) Heating at  $210^\circ\text{C}$ . for one hour.

When any reaction occurred, the usual result was a deposit of non-volatile yellow solid, and recovery of unused reactants. In some cases, fair yields of  $(\text{CF}_3)_2\text{PH}$  were observed, as in one experiment employing iodine as a catalyst under 36-hour exposure to bright sunlight. The parallel experiment, wherein 4.597 mmoles of  $\text{CF}_3\text{I}$  and 2.603 mmoles of  $\text{CH}_3\text{HPP}(\text{CF}_3)_2$  were exposed in the same way without iodine, produced a yellow solid which dissolved during three hours at  $110^\circ\text{C}$ .; then after six hours at  $110^\circ\text{C}$ . the clear yellow solution was cooled to  $25^\circ\text{C}$ . and separated into two liquid phases, yellow above and dark orange below. As the volatiles were removed the non-volatile solid reappeared. The yield of  $(\text{CF}_3)_2\text{PH}$  was 1.588 mmoles (60%), along with 2.286 mmoles of unused  $\text{CF}_3\text{PI}$  and a trace of  $\text{HCF}_3$ .

It was considered possible that a Lewis acid would have catalytic value through attachment to the more basic phosphorus atom of the biphosphine, and in particular, that a trace of  $\text{CH}_3\text{PH}_3\text{I}$  remaining in the biphosphine might have served as a source of HI to promote the previously reported uniquely successful reaction. However, when  $\text{CF}_3\text{I}$  and  $\text{CH}_3\text{HPP}(\text{CF}_3)_2$  were irradiated by sunlight during three days, in the presence of a small sample of  $\text{CH}_3\text{PH}_3\text{I}$ , the results were essentially the same as before: a nearly 60% yield of  $(\text{CF}_3)_2\text{PH}$  and the usual non-volatile yellow solid, plus a trace of  $\text{HCF}_3$ . Again there was no appreciable yield of  $\text{CH}_3\text{CF}_3\text{PI}$ , and it was decided that this  $\text{CF}_3\text{I}-\text{CH}_3\text{HPP}(\text{CF}_3)_2$  approach must be written off as unpromising.

## 2. Depolymerization of $(\text{CF}_3\text{P})_n$ Rings by Methyl Iodide

Some of the previously-reported experiments on the addition of  $\text{CH}_3\text{I}$  to a mixture of  $(\text{CF}_3\text{P})_4$  and  $(\text{CF}_3\text{P})_5$  had produced good percent yields of  $\text{CH}_3\text{CF}_3\text{PI}$ , but only under conditions such that the percent conversion was low (Ref. 2, p. 177). We now have tried four more experiments on the subject, adding more lore to the previous tabulation of results, but with no significant advance in the efficiency of this very tricky process. The new results are shown in Table XXVII.

For all of these experiments very small sealed tubes were employed so that the reactants would remain primarily in the liquid phase. It was noted that the  $(\text{CF}_3\text{P})_4$  initially was not all dissolved, but remained in solution after cooling from a  $110^\circ\text{C}$ . heating. In all cases the onset of reaction was signalled by a yellow coloration, later darkening as a non-volatile tarry brown solid was formed. It is apparent from the results that little reaction occurs at temperatures below about  $140^\circ\text{C}$ ., whereas much destruction of the desired product occurs when the tube is heated at temperatures scarcely  $20^\circ\text{C}$ . higher.



TABLE XXVII

Further Experiments on the  
 $\text{CH}_3\text{I}-(\text{CF}_3\text{P})_n$  Reaction

Expt. No.	Time (hrs.)	Temp. (°C.)	CF <sub>3</sub> P units (mmoles)		CH <sub>3</sub> I (mmoles)		%CF <sub>3</sub> P used up	%yield CF <sub>3</sub> PI <sub>2</sub>	%yield CH <sub>3</sub> CF <sub>3</sub> PI
			start	end	start	end			
10	17	110	3.106	- -	4.047	- -	nil	nil	nil
	21	138	- -	3.041	- -	3.884	2.1	nil	nil
	4.5	158	- -	0.528	- -	2.753	82.6	49	14 <sup>a</sup>
11	2	158	1.948	0.427	3.745	2.408	78.1	20	(trace)
12	33	138	4.941	- -	7.592	- -	(trace)	nil	nil
	6	158	- -	?	- -	3.745	?	(obsd.)	14 <sup>b</sup>
13	5	152 <sup>c</sup>	4.823	- -	5.161	- -	- -	- -	- -
	3	196	- -	1.370	- -	0.02	71.6	22	nil

<sup>a</sup>Based on CF<sub>3</sub>P units consumed; 33% based on CH<sub>3</sub>I consumed.

<sup>b</sup>Based on CH<sub>3</sub>I consumed.

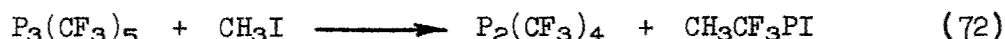
<sup>c</sup>Brown oil forming; tube not opened.



The need for a more efficient procedure is obvious. Hence we are hoping soon to return to the task of improving one of our earliest methods of making  $\text{CH}_3\text{CF}_3\text{P}$  compounds--the addition of  $\text{CH}_3\text{I}$  to  $(\text{CH}_3)_3\text{PPCF}_3$  and treatment of the product with  $\text{HCl}$  (Ref. 11, p. 95). We have made some exploratory trials of the parallel process using  $(\text{CH}_3)_3\text{NPCF}_3$ , but minor impurities seemed to interfere seriously with the clean formation of this monomer-adduct, and it probably does not capture  $\text{CH}_3\text{I}$  so readily as  $(\text{CH}_3)_3\text{PPCF}_3$  does.

### 3. The Triphosphine Approach

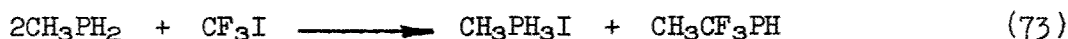
Since  $\text{P}_3(\text{CF}_3)_5$  decomposes to  $\text{P}_2(\text{CF}_3)_4$  and  $(\text{CF}_3\text{P})_n$ , the reaction indicated by Equation 72 seemed possible.



The mechanism could be through direct attachment of the  $\text{CH}_3$  group to the central phosphorus atom (which could be more basic than the end P atoms), or the  $\text{CH}_3$  group might add as bonds were broken during the decomposition. Also, the relative active  $(\text{CF}_3)_2\text{P}$  groups might react with more  $\text{CH}_3\text{I}$  to make  $(\text{CF}_3)_2\text{PI}$  and  $(\text{CF}_3)_2\text{PCH}_3$ , as  $\text{P}_2(\text{CF}_3)_4$  itself fails to do. However, a mixture of  $\text{P}_3(\text{CF}_3)_5$  and  $\text{CH}_3\text{I}$  would not even mix at room temperature, and in a pentane solution at  $65^\circ\text{C}$ . the only reaction was decomposition of one-fourth of the  $\text{P}_3(\text{CF}_3)_5$ . Thus more drastic heating would not be useful. It appears that  $\text{P}_3(\text{CF}_3)_5$  has scarcely more base action than  $\text{P}_2(\text{CF}_3)_4$ .

### 4. Trifluoromethylphosphine with Methyl Iodide

A possible obverse to the previously-reported (Ref. 2, p. 179) fairly successful but slow process (Equation 73) would be the reaction indicated by Equation 74, possibly with  $(\text{CH}_3)_3\text{N}$  to remove the  $\text{HI}$ .



However, the reaction failed to occur even during four days at room temperature, and with the amine added, the only reaction was the formation of  $(\text{CH}_3)_4\text{NI}$ .

### D. The Quest for an Open-Chain Tetrphosphine

The all-phosphorus rings in  $(\text{CF}_3\text{P})_4$  and  $(\text{CF}_3\text{P})_5$  have been opened by water or various alcohols to form oxy-polyphosphines and the hydrogen-terminated chains  $(\text{CF}_3\text{PH})_2$  and  $\text{H}_2(\text{CF}_3\text{P})_3$  (Ref. 9, pp. 98-104). It seems reasonable to assume that the first step in such a process is the formation of an open  $(\text{CF}_3\text{P})_n$  chain with H on one end and OR on the other; then a similar P-P bond cleavage in a random manner at various points on the chain would account for all observed products. By this argument, a delicate alcoholysis of  $(\text{CF}_3\text{P})_5$  should form first



the open-chain pentaphosphine  $\text{H}-\text{P}(\text{CF}_3)-\text{P}(\text{CF}_3)-\text{P}(\text{CF}_3)-\text{P}(\text{CF}_3)-\text{OR}$ . Then a similar attack at the

$\text{P}-\text{POR}$  bond would have a 50% probability of forming the open-chain tetraphosphine  $\text{H}_2(\text{CF}_3\text{P})_4$ . Assuming that the four P-P bonds would have equal probability of alcoholic cleavage, the theoretical yield of this tetraphosphine would be one molecule per eight  $(\text{CF}_3\text{P})_5$ . At the same time there would be considerable formation of  $(\text{CF}_3\text{PH})_2$ ,  $\text{H}_2(\text{CF}_3\text{P})_3$ , and various alkoxyphosphines. However, even with such a low prospective yield, it seemed desirable to seek the tetraphosphine  $\text{H}_2(\text{CF}_3\text{P})_4$  and to learn something of its degree of instability.

### 1. Exploratory Alcoholysis Experiments

For the initial experiments on the alcoholysis, the pentamer  $(\text{CF}_3\text{P})_5$  was made from the tetramer by trimethylphosphine-catalysis in ether solution, as recently suggested by our erstwhile colleague Dr. Walter Mahler. A solution containing 10.32 mmoles of  $\text{CF}_3\text{P}$  units with 0.028 mmole of  $(\text{CH}_3)_3\text{P}$  in 1.486 g. of diethyl ether gave a 34% yield of the pentamer after 36 days at room temperature. The process doubtless would have gone farther and faster with a higher concentration of the catalyst at a higher temperature. The process is feasible only with highly purified materials, for traces of some impurities can cause splitting of the ether and the formation of dark non-volatile products.

The initial experiments with  $(\text{CF}_3\text{P})_5$  and equimolar proportions of methanol in ether at room temperature showed major formation of relatively light products, with much pentamer recovered. It appeared that the initially-formed  $\text{H}(\text{CF}_3\text{P})_5\text{OCH}_3$  was more easily cleaved than the pentamer itself. In the hope of modifying this effect, t-butanol was tried instead of  $\text{CH}_3\text{OH}$ . However, this led to greater difficulty in resolving the mixed products: the triphosphine  $\text{H}_2(\text{CF}_3\text{P})_3$  was not easily separated from the butoxy-polyphosphines; and a possible  $\text{H}_2(\text{CF}_3\text{P})_4$  could not be isolated from the dibutoxyphosphines which probably were present.

To lower the volatility of the alkoxyphosphines, we next tried the use of n-heptanol, assuming that even the simplest heptoxyphosphine,  $\text{C}_7\text{H}_{15}\text{OPHCF}_3$ , would be less volatile than the desired tetraphosphine. Then it should be possible to do the alcoholysis in a fractionating column so as to take off the tetraphosphine as rapidly as it might be formed, and so avoid its destruction by further alcoholysis. This method was obviously sound in principle, but the heptoxyphosphine product still was too volatile for the best results, so that hydrocarbon material appeared in the infrared spectrum of the pertinent fractions. Hence we finally chose to use lauryl alcohol ( $n\text{-C}_{12}\text{H}_{25}\text{OH}$ ), and this led to actual evidence of the formation of the desired  $\text{H}_2(\text{CF}_3\text{P})_4$ .

### 2. The Lauryl Alcohol Reaction

Lauryl alcohol was put into the boiler of a reflux column and thoroughly degassed under high vacuum. Then a 1.689 mmole sample of  $(\text{CF}_3\text{P})_5$  was brought in by condensation at a low temperature, and the mixture was heated at 30-40°C. with the reflux chamber at -5°C. The volatile products trapped under high vacuum at -23 and -45°C. were examined further. The -23°C. fraction had approximately the volatility of  $(\text{CF}_3\text{P})_4$  (1.57 mm. at 19.0°C. vs. the known value, 1.42 mm. at 19.2°C.) and did not clearly show the P-H stretching mode in the



infrared spectrum. However, the  $-45^{\circ}\text{C}$ . fraction definitely showed P-H stretching, which persisted after part of the sample had decomposed to more volatile phosphines. Thus it appeared that the desired tetraphosphine  $\text{H}_2(\text{CF}_3\text{P})_4$  might be present, and enough more volatile than  $(\text{CF}_3\text{P})_4$  for feasible isolation.

A second experiment, using 1.876 mmoles of lauryl alcohol and 0.961 mmole of  $(\text{CF}_3\text{P})_5$ , was carried on at  $22^{\circ}\text{C}$ . with the reflux head at  $-15^{\circ}\text{C}$ . The effluent was led directly through traps under high vacuum at  $-23$  and  $-196^{\circ}\text{C}$ , and the  $-23^{\circ}\text{C}$ . fraction was returned at intervals to the boiler. After six hours of such operation, the process was halted and the  $-196^{\circ}\text{C}$ . condensate was further fractionated. Again there was evidence of P-H material less volatile than either  $(\text{CF}_3\text{PH})_2$  or  $\text{H}_2(\text{CF}_3\text{P})_3$ , both of which were formed when it decomposed (especially the latter). It was quite distinctly more volatile than  $(\text{CF}_3\text{P})_5$ , and seemed quite free of  $(\text{CF}_3\text{P})_4$ . It was not much affected by a 15-hour contact with mercury, but was extensively destroyed by a 10-minute contact with Apiezon L grease.

The reflux-lauryliolysis was repeated on a considerably larger scale, with halocarbon grease lubricating all stopcocks having any contact with the vapors. The lauryl alcohol (2.1 g.) was pretreated with  $(\text{CF}_3\text{P})_5$  and pumped free of volatiles; then it was allowed to react with 1.382 g. of pure  $(\text{CF}_3\text{P})_5$ , with column-reflux for six hours. No  $\text{CF}_3\text{PH}_2$  resulted, but it was possible to isolate 42.4 mg. of  $(\text{CF}_3\text{PH})_2$ . The fractionation of the sample containing the desired tetraphosphine seemed to be disturbed by its decomposition. Thus the initial yield of  $\text{H}_2(\text{CF}_3\text{P})_3$  probably was 300 mg., but at least 50 mg. more came from further manipulation of the tetraphosphine fraction. The final yield of purified tetraphosphine was close to 31 mg., after considerable loss by decomposition and by rejection of fractions from which its isolation would have been difficult.

After the delivery of the tetraphosphine from the column, the residue was left for six weeks at room temperature. It is assumed that it contained all of the possible alkoxyphosphines of type formulas  $\text{H}(\text{CF}_3\text{P})_n\text{OR}$  and  $\text{RO}(\text{CF}_3\text{P})_n\text{OR}$  accounting for the formation of the three known phosphines  $\text{CF}_3\text{PH}_2$ ,  $(\text{CF}_3\text{PH})_2$ , and  $\text{H}_2\text{P}(\text{CF}_3\text{P})_3$  by further alcoholysis. Also found was a fraction even more volatile than  $\text{CF}_3\text{PH}_2$ , but with an infrared spectrum showing the presence of a  $\text{CF}_3$  group. A band at  $1029\text{ cm}^{-1}$  might indicate P-H bending, but for the present we have no opinion of the identity of this component.

### 3. Isolation of the Tetraphosphine

The main portion of the presumed tetraphosphine passed a high-vacuum trap at  $-23^{\circ}\text{C}$ . and condensed out at  $-30^{\circ}\text{C}$ . Its vapor tension at  $25^{\circ}\text{C}$ . was measured as 5 mm. in the all-glass spoon-gauge system, contrasting with 0.6 mm. for  $(\text{CF}_3\text{P})_5$  and 16 mm. for  $\text{H}_2(\text{CF}_3\text{P})_3$ . However, two molecular weight measurements (347 and 348) indicated the presence of a considerable proportion of the triphosphine. In order to eliminate this, a sample was fractionally condensed at a slightly higher pressure, in the trap at  $-23^{\circ}\text{C}$ . and then further high-vacuum distilled at that temperature. Thus it was possible to obtain a 30.6 mg. fraction having molecular weight 424 in the spoon-gauge system at  $71^{\circ}\text{C}$ .; calcd. value for  $\text{H}_2(\text{CF}_3\text{P})_4$ , 402. Further measurements soon gave lower values, such as 351 at  $81^{\circ}\text{C}$ . or 379 at  $71^{\circ}\text{C}$ ., corresponding to decomposition which was not avoidable at temperatures high enough for vapor-phase determinations.



#### 4. Analysis

An attempt at a quantitative decomposition of the presumed tetraphosphine to known phosphines by nickel catalysis did not succeed, apparently because an optimum nickel surface was not present. However, it was possible to demonstrate the composition of the sample by a long process of decomposition in the presence of mercury, at temperatures as high as 150°C. The repurified 25.6 mg. sample thus yielded 0.054 mmole of  $\text{CF}_3\text{PH}_2$ , 3.7 mg. of material having the properties of  $(\text{CF}_3\text{PH})_2$ , and 15.1 mg. of a mixture of  $(\text{CF}_3\text{P})_4$  and  $(\text{CF}_3\text{P})_5$ . Thus the total of  $\text{CF}_3\text{P}$  units amounted to 0.242 mmole (calcd., 0.255) and 0.127 mg. atoms of H (calcd., 0.128). These results, taken with the roughly determined molecular weight and the volatility, leave little doubt of the formula  $\text{H}_2(\text{CF}_3\text{P})_4$ ; however, for proper study of the physical properties of this new substance, it will be necessary to make it in larger quantity and purify it more thoroughly, especially for elimination of its decomposition products. For good results, it will be necessary to work with a completely grease-free vacuum system, not involving mercury. Mercury definitely catalyzed its decomposition, and even the halocarbon grease affects it to some degree.

#### E. Alternative Polyphosphine Syntheses

##### 1. Synthesis of $\text{CF}_3\text{P}$ Polymers in Solution

The pentamer  $(\text{CF}_3\text{P})_5$  gains stability relative to the tetramer when both are in solution, so that it seemed possibly advantageous for the synthesis of the pentamer if the  $\text{CF}_3\text{PI}_2$  were reduced in a solvent. Accordingly, the action of mercury on an ether solution of  $\text{CF}_3\text{PI}_2$  was tried, but the rate of reaction decreased so sharply as the concentration of  $\text{CF}_3\text{PI}_2$  was lowered by the reaction, that it became very difficult to complete the process. The reaction again was incomplete when a benzene solution of  $\text{CF}_3\text{PI}_2$  was heated with powdered antimony for six hours at 85°C. with frequent shaking. With incomplete reaction, it becomes difficult to isolate the  $(\text{CF}_3\text{P})_4$  and  $(\text{CF}_3\text{P})_5$  from the unused  $\text{CF}_3\text{PI}_2$ .

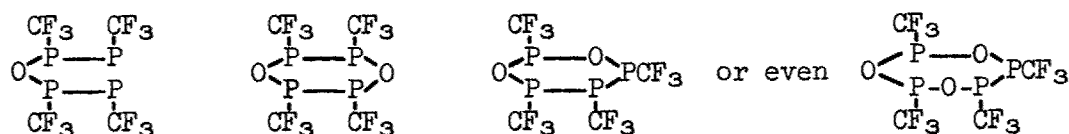
##### 2. A Probable Oxy-Polyphosphine

For these reductions in solution, the  $\text{CF}_3\text{PI}_2$  samples had been derived from the  $\text{AgCO}_2\text{CF}_3\text{-P}_X\text{-I}_2$  process, meaning that oxyphosphine impurities probably were present. A by-product apparently resulting from some such impurity was a slightly volatile white crystalline material, melting between 72 and 80°C. and having vapor tensions 5.5 mm. at 80°C., 22.7 mm. at 103°C., and 48.7 mm. at 123.5°C. These properties do not correlate with a single substance in high purity, but the molecular weights of various fractions were fairly consistent: 446, 449, 442, and 438. The material seemed to be unaffected by air, although oxidation to  $(\text{CF}_3\text{PO}_2)_n$  polymers might have escaped notice; but then it also failed to react with concentrated aqueous hydrochloric acid, which would have hydrolyzed that polymer. Indeed, after the exposure to  $\text{HCl}\cdot\text{H}_2\text{O}$ , it was recovered as a sublimate. Nitric acid dissolved it, probably with extensive oxidation. Tests for mercury and antimony, on a brominated sample, were negative.

It now seems most probable that the main component of this by-product was an oxidized polyphosphine of some interesting type. It is difficult



to suggest a most probable formula, for the molecular weight results could have been influenced by some trace of pentameric  $\text{CF}_3\text{P}$ , which also could help to account for an infrared spectrum having more multiplicity of C-F stretching bands than could be accounted for by a single situation of the  $\text{CF}_3$  groups. Thus our present limited knowledge permits the consideration of a number of possible oxy-polyphosphine structural patterns, such as the following.



A direct quest for any of these compounds would be quite interesting, but should not be given priority over the attempt to make  $(\text{CF}_3\text{PO})_n$  polymers.

### 3. Attempts at Direct Introduction of Phosphorus

It was considered possible that either  $(\text{CF}_3)_2\text{PI}$  or  $\text{P}_2(\text{CF}_3)_4$  would react with white phosphorus to produce interesting new polyphosphines, or at least to form  $(\text{CF}_3\text{P})_n$  rings more conveniently. However, it appears that the projected reactions do not occur at temperatures low enough for open-chain polyphosphines to be stable, and some undesired effects occur too easily. For example,  $(\text{CF}_3)_2\text{PI}$  with  $\text{P}_4$  during four days at  $80^\circ\text{C}$ . reacted to form some  $\text{CF}_3\text{I}$  while some of the  $\text{P}_4$  went to red phosphorus; the consumption of the  $(\text{CF}_3)_2\text{PI}$  was only 8%. The attempt with  $\text{P}_2(\text{CF}_3)_4$  and  $\text{P}_4$ , during four days at  $125^\circ\text{C}$ ., showed little effect except a red coloration and the formation of a trace of  $(\text{CF}_3)_3\text{P}$ .



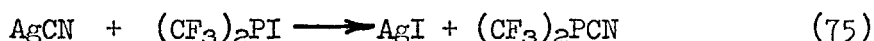
#### IV. Cyano-Phosphine Chemistry

Compounds of the types  $R_2PCN$  and  $RP(CN)_2$  offer a number of interesting possibilities for polymer purposes. For example, the polymerization of the CN group to the  $(CN)_3$  cyanuric ring would convert  $R_2PCN$  to a strongly-connected triphosphine which could be used to make mechanically superior P-B-H resins. Or the same polymerization of both CN groups in  $RP(CN)_2$  would lead directly to resins which would be expected to have high stability. Another possibility would be the use of diborane for hydroboration of these types, leading to resinous materials involving  $(BN)_3$  rings of either the borazine type or the less hydroborated Schiff-base-borine unit. For thermally stable resins,  $B_5H_9$  could be employed to the same general purpose.

The  $R_2PCN$  polymerization was attempted through the use of  $(CF_3)_2PCN$ , since the cyanogen halide series indicates that electronegativity aids the polymerization of the CN group. Even so, we have not succeeded in catalyzing the polymerization of this compound. However, diborane reacts well enough with this compound, and the resulting material has a very promising resinous character.

##### A. Syntheses and Characterizations

The little-known compound  $(CF_3)_2PCN$  was reported first from the University of Cambridge in 1953, along with its b.p. ( $48^\circ C.$ ), refractive index, and infrared spectrum.<sup>12</sup> Its synthesis was based upon the reaction



We chose to begin with a new approach: the cleavage of the P-P bond of  $P_2(CF_3)_4$  by I-CN. One reason for this was the hope of exploring this P-P bond cleavage in relation to the possibility of making open-chain cyano-polyphosphines from  $(CF_3P)_n$  polymers. A further justification, emerging later, was the erratic character of the original synthesis: depending upon the physical character of the AgCN sample, one might get a very high yield of  $(CF_3)_2PCN$  or virtually none at all.

1. Characterization of Reactants. For our process the ICN was made by the usual reaction of iodine with sodium cyanide in aqueous solution, and purified first by recrystallization from chloroform and then by sublimation into the reaction tube. It was quite colorless and melted at  $146^\circ C.$  (known m.p.,  $146.5^\circ C.$ ).

The  $P_2(CF_3)_4$  sample was purified by column fractionation under high-vacuum, and its vapor tensions were measured over a wide temperature range for the first time. The results, given with the equation in Table XXVIII, correspond to b.p. =  $83.8^\circ C.$  (literature,  $83-84^\circ C.$ )<sup>12</sup> and Trouton constant =  $22.4 \text{ cal./deg.mole.}$  The three lowest pressures, represented by the averaged  $-24^\circ C.$  datum, deviate about 10% above the calculated values, suggesting a trace of a more volatile impurity, possibly arising from grease-induced decomposition.

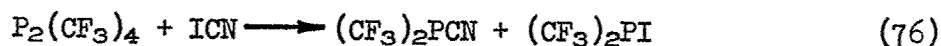


TABLE XXVIII

Vapor Tensions of Liquid  $P_2(CF_3)_4$   
 $(\log P_{\text{mm}} = 5.0615 + 1.75 \log T - 0.003500T - 1927/T)$

t (°C.)	-24.0	-10.9	-5.9	0.00	12.3	22.1	30.1	39.7
$P_{\text{mm}}$ (obsd.)	4.84	10.68	14.6	20.4	40.5	67.1	98.3	149.2
$P_{\text{mm}}$ (calcd.)	4.46	10.68	14.6	20.5	40.7	66.8	97.5	149.3

2. Synthesis of  $(CF_3)_2PCN$ . The reaction of 0.455 mmole of ICN with 0.414 mmole of  $P_2(CF_3)_4$  began very slowly at room temperature (yellowing of the ICN surface), but approached completion during 5 hours at 80-90°C. The resulting all-liquid mixture was high-vacuum distilled to isolate the  $(CF_3)_2PCN$ , the final purification of which required shaking with mercury to convert the last of the  $(CF_3)_2PI$  to  $P_2(CF_3)_4$ . The yield of  $(CF_3)_2PCN$  was only 0.18 mmole, or 43% of that calculated from the equation



However, the actually isolated yield of  $(CF_3)_2PI$  was 0.336 mmole, or 81%; thus if we allow for the conversion of some of it to  $P_2(CF_3)_4$ , the actual yield was nearly quantitative. It would be reasonable to attribute the low yield of  $(CF_3)_2PCN$  to polymerization, but the question whether the nonvolatile by-product was a cyanuric triphosphine or other polymer remains to be decided. Also, some minor volatile by-products have not been identified. Thus it appears that any use of cyanogen iodide for cleavage of P-P bonding in the  $(CF_3P)_n$  ring polymers is likely to encounter complications which need to be fully understood before that relatively complex task is attempted.

The original method of synthesis of  $(CF_3)_2PCN$  also has been studied. Even with very pure silver cyanide the reaction sometimes gave



very poor yields or even failed to occur more than slightly. For example, a sample of AgCN which had been recrystallized from concentrated aqueous ammonia, and then dried and well powdered, gave only 5-10% yields. On the other hand, a silver cyanide sample which seemed essentially amorphous (i.e., an ultramicro-crystalline precipitate) gave yields above 90%. Access of the  $(\text{CF}_3)_2\text{PI}$  to the surface of the solid AgCN evidently is the governing factor.

3. Volatility of the Mono-cyanophosphine. The original report of  $(\text{CF}_3)_2\text{PCN}$ <sup>2</sup> gave no vapor-tension data, such as we now have obtained for a well purified sample. These results, shown in Table XXIX with an equation, imply the normal b.p. to be 46.1°C., the molar enthalpy of vaporization 7511 cal., and the Trouton constant 23.53 cal./deg.mole. This relatively high value of the Trouton constant suggests a tendency toward liquid-phase association. This could be due to a CN-P donor bonding, such as would also account for a noticeable tendency toward instability.

TABLE XXIX

$$\text{Vapor Tensions of Liquid } (\text{CF}_3)_2\text{PCN}$$

$$(\log P_{\text{mm}} = 5.2225 + 1.75 \log T - 0.003660T - 1773/T)$$

t (°C.)	-45.4	-31.2	-23.7	-17.1	-9.1	0.1	12.3	19.4
P <sub>mm</sub> (obsd.)	5.37	15.08	24.98	37.58	60.22	99.0	183.7	255.4
P <sub>mm</sub> (calcd.)	5.37	15.16	24.94	37.65	60.20	99.5	183.6	255.4

4. Attempts to Polymerize the Cyanophosphine. It is well known that HCl causes rapid polymerization of ClCN and even HCN condenses to larger molecules in the presence of HCl; hence the same catalyst was tried for the polymerization of  $(\text{CF}_3)_2\text{PCN}$ . However, HCl seemed to have no effect upon this cyanophosphine, either at room temperature or at 80°C. Even after being heated at 150°C., nearly all of a sample of  $(\text{CF}_3)_2\text{PCN}$  was recovered, having formed only a trace of an unidentified more volatile material. Possibly an effective polymerization catalyst can be found, but it may be that the  $(\text{CF}_3)_2\text{P}$  group has an effect more like iodine in ICN, which also is difficult to polymerize.



5. The Cyanophosphine-Diborane Reaction. Unlike  $\text{CH}_3\text{CN}$ , which absorbs diborane fairly rapidly at low temperatures to make  $\text{CH}_3\text{CN}\cdot\text{BH}_3$  (reversibly) and then more slowly undergoes transfer of H from B to C,  $(\text{CF}_3)_2\text{PCN}$  reacts with diborane not at all at  $-78^\circ\text{C}$ ., scarcely at  $-30^\circ\text{C}$ ., and only very slowly and incompletely at  $0^\circ\text{C}$ . At  $23^\circ\text{C}$ ., however, diborane in excess destroyed all available  $(\text{CF}_3)_2\text{PCN}$  in three hours. In such reactions the expected 2:1 ratio, corresponding to the formula  $(\text{CF}_3)_2\text{PCN}\cdot\text{BH}_3$ , occurs only fortuitously, by a balance of various effects, such as excess use of diborane and some formation of  $(\text{CF}_3)_2\text{PH}$  and  $\text{P}_2(\text{CF}_3)_4$ . Table XXX summarizes three experiments, with quantities in mmoles.

TABLE XXX

The  $(\text{CF}_3)_2\text{PCN-B}_2\text{H}_6$  Reaction

Expt. No.	Time (hrs.)	Temp. ( $^\circ\text{C}$ .)	Diborane start used	$(\text{CF}_3)_2\text{PCN}$ start used	$(\text{CF}_3)_2\text{PH}$	$\text{P}_2(\text{CF}_3)_4$	Residue Formula
1	14	0	0.344 0.265	0.659 0.602	0.065	0.039	$\text{P}_2\text{B}_{2.9}\text{C}_{2.7}$
2	3	23	0.755 0.147	0.282 all	?	0.04	$\text{P}_2\text{B}_{2.9}\text{C}_{2.6}$
3	20	22	1.592 0.678	1.194 all	0.033	0.120	$\text{P}_2\text{B}_{2.3}\text{C}_{2.6}$

Here the residue formulas are given with  $\text{P} = (\text{CF}_3)_2\text{P}$ ,  $\text{B} = \text{BH}_3$ , and  $\text{C} = \text{CN}$ . In Experiment 1 the recovered  $(\text{CF}_3)_2\text{PCN}$  was accompanied by another cyanide-containing material which has not been identified. It amounted to 0.02 mmole.

The nonvolatile residues of such experiments were glassy yellow solids which seemed to be unaffected by the open air, except possibly on the surface. The material from Experiment 1 was hydrolyzed in sodium hydroxide, with a Kjeldahl-type delivery of the volatile base, amounting to 0.36 mmole. This represented 60% of the original CN groups. A test for methylamine by the chloroform-alkali method was negative.

The residue from Experiment 2 was heated to  $160^\circ\text{C}$ . under high vacuum, yielding nothing volatile. Next it was hydrolyzed in hydrochloric acid during 12 hours at  $120^\circ\text{C}$ ., without breaking down completely: the remaining white solid also failed to dissolve in dilute or concentrated nitric or sulfuric acid, or in aqueous sodium hydroxide. The volatile hydrolysis products (in mmoles) were  $0.105\text{H}_2$ ,  $0.121\text{HCF}_3$ ,  $0.022(\text{CF}_3)_2\text{PH}$ ,  $0.035\text{CF}_3\text{PH}_2$ . Titration of



the main hydrolysis solution now showed that none of the HCl had been consumed, but boric acid ran low: 0.24 mmole vs. calcd. 0.294 mmole. A test for volatile base was positive but the quantity was not determined.

The unheated residue from Experiment 3 proved easier to hydrolyze completely. With plain water, the process was well advanced during a fairly short time at room temperature, and when it became slow, a heating in a sealed tube for two days at 120° brought it close to completion. The volatile hydrolysis products are listed in Table XXXI, in mmoles.

TABLE XXXI

Volatile Hydrolysis Products from the  $(\text{CF}_3)_2\text{PCN-B}_2\text{H}_6$  Reaction (Expt. 3)

	$\text{H}_2$	$\text{HCF}_3$	$\text{CF}_3\text{PH}_2$	$(\text{CF}_3)_2\text{PH}$
Room temperature	0.802	0.131	nil	0.071
At 120°C.	<u>0.523</u>	<u>0.839</u>	<u>0.195</u>	<u>0.063</u>
Sum	1.325	0.970	0.195	0.134

An interesting feature of this experiment was the formation of a yellow oil by room-temperature hydrolysis. It was the hydrolysis of this material which gave the results in the 120°C. line of Table XXXI. A similar oil from another experiment was hydrolyzed only after five hours at 140°C.

The aqueous hydrolysate from Experiment 3 contained an acid, requiring 0.943 meq. of NaOH for titration to pH 6. Then the boron titration gave 1.005 mmoles of  $\text{B}(\text{OH})_3$ , vs. calcd. 1.356 mmoles of  $\text{BH}_3$  absorbed by the cyanophosphine in the original reaction. A Kjeldahl-type distillation delivered 0.76 mmole of volatile base, meaning that 64% of the CN nitrogen had been reduced by the boron-hydride reaction.

Although the boron titration ran low, it is interesting that the delivery of hydrogen by hydrolysis corresponded nearly to one  $\text{H}_2$  per  $\text{BH}_3$  group originally absorbed, as though reduction to the  $(\text{RNBH})_3$  stage had occurred. However, this result may be somewhat fortuitous; there is room for consideration



of the  $\text{RCHC=NBH}_2$  stage as a component of the polymer, as well as  $(\text{BN})_3$  and  $(\text{CN})_3$  rings and some  $(\text{BH})_x$  polymer principle. This polymer might be quite interesting, but its thermal stability and other useful properties have not yet been investigated.

6. Trifluoromethyl-bis(cyano)phosphine. A sample of  $\text{CF}_3\text{PI}_2$  was allowed to react with  $\text{AgCN}$  in a sealed tube. The main product of the reaction was a colorless liquid, condensing completely in a high-vacuum trap at  $-45^\circ\text{C}$ . and having 4.1 mm. vapor tension at  $0^\circ\text{C}$ . Its spectrum (Infracord instrument) showed the typical  $\text{C}\equiv\text{N}$  stretching frequency near  $2200\text{ cm}^{-1}$  and the trio of strong peaks typical of a single  $\text{CF}_3$  group on phosphorus. Its molecular weight (147) corresponds well enough to the expected formula  $\text{CF}_3\text{P}(\text{CN})_2$  (calcd., 152), but this is yet to be confirmed by analysis.



## V. Summary

The infrared spectra of  $[(CH_3)_2PBH_2]_3$ ,  $[(CH_3)_2PBD_2]_3$ ,  $(CH_3CF_3PBH_2)_3$ ,  $[(CF_3)_2PBH_2]_3$ ,  $[(CF_3)_2PBD_2]_3$ , and  $[(CH_3)_2NBH_2]_3$  have been recorded by precision instruments, with results indicating the  $BH_2$  wagging frequencies increase more rapidly than the  $BH_2$  rocking frequencies, as  $CH_3$  is replaced by  $CF_3$ . Thus it appears that the  $HBH$  bond angle widens as phosphorus becomes more electronegative and less basic. Of this series of compounds,  $(CH_3CF_3PBH_2)_3$  is novel, having been formed in a very small yield from the unstable adduct  $CH_3CF_3PH \cdot BH_3$ . This in turn was made from the virtually new phosphine  $CH_3CF_3PH$  (b.p. est.  $17.94^\circ C.$ ). The  $CH_3$  frequencies for  $[(CH_3)_2NBH_2]_3$  indicate strong mutual interference by methyl groups in the axial positions on the cyclohexane-type ring--an effect not found for any of the  $R_2PBH_2$  trimers.

A more accurate infrared spectrum for  $(CF_3HPOOH)_2$ , taken with the vapor-phase dissociation pressures, confirms the phosphinic-acid dimer structure. Compounds having  $P-OCCF_3$  bonds tend to dissociate to  $P-O-P$  compounds and  $(CF_3CO)_2O$ , indicating a new approach to this kind of polymer bonding. The new compound  $(CF_3)_2POCCF_3$  (m.p. near  $-75^\circ C.$ ; 58 mm. at  $0^\circ C.$ ) was made from  $AgCO_2CF_3$  and  $(CF_3)_2PI$ . It dissociates reversibly to  $(CF_3)_2POP(CF_3)_2$  and  $(CF_3CO)_2O$ , with a formation constant  $K = 9$  at temperatures near  $25^\circ C.$  The reaction of  $AgCO_2CF_3$  with  $CF_3PI_2$  gives a high yield of  $(CF_3CO)_2O$ , presumably by a virtually irreversible condensation of the initially-formed  $CF_3P(OCCF_3)_2$  through intermediates such as  $CF_3COOP-O-P(OCCF_3)_2$  to  $(CF_3PO)_n$  polymers. In

relation to this work, pure  $(CF_3)_2PI$  was made from  $P_2(CF_3)_4$  and  $HgCl_2$  was used to make pure  $(CF_3)_2PCl$  and  $CF_3PCl_2$  from the iodides; then the infrared spectra were recorded in a precise manner and the vapor tensions were measured accurately. Gaseous  $(CH_3)_3P$  completely converts solid  $(CF_3P)_4$  to  $(CH_3)_3PPCF_3$  ( $\Delta F^\circ = 13.82 - 0.0384T$  kcal. for the reverse process); but this adduct is incompletely formed in  $(CH_3)_3P$  solutions. Catalytic conversion of  $(CF_3P)_4$  to  $(CF_3P)_5$  is favored in solution.

The first open-chain tetraphosphine,  $H_2(CF_3P)_4$ , was made from  $(CF_3P)_5$  and  $C_{12}H_{25}OH$  in a reflux column. It decomposes easily to  $(CF_3)_2PH$ ,  $(CF_3PH)_2$ ,  $H_2(CF_3)_3$ , and  $(CF_3P)_n$  rings. The synthesis of  $(CF_3P)_n$  from  $CF_3PI_2$  in solution is difficult to complete, but with  $P-O$  impurities a probably oxy-tetraphosphine is observed.

The new triphosphine  $P_3(CF_3)_5$  (b.p. above  $130^\circ C.$ ) can be made from  $(CF_3)_2PI$  or  $(CF_3)_2PCl$  with  $CF_3PH_2$  and  $(CH_3)_3N$ , probably with  $CF_3HPP(CF_3)_3$  as an intermediate. It has an ultraviolet peak at  $2210 \text{ \AA}$ . and its infrared spectrum conforms to expectations. It decomposes to  $P_2(CF_3)_4$  and  $(CF_3P)_n$ , and is seriously affected by hydrocarbon greases.

Attempts to make  $CH_3CF_3PI$  from  $CH_3HPP(CF_3)_2$  and  $CF_3I$  have failed, and the  $(CF_3P)_n-CH_3I$  process still is difficult. The dissociation of  $P_3(CF_3)_5$  in the presence of  $CH_3I$  gave no  $CH_3CF_3PI$ , and an attempt to add  $CH_3I$  to  $CF_3PH_2$  also failed.



The compound  $(\text{CF}_3)_2\text{PCN}$  (b.p.  $46^\circ\text{C}$ ., possibly slightly associated) has been made both by the somewhat variable literature method and by a new reaction between  $\text{ICN}$  and  $\text{P}_2(\text{CF}_3)_4$  (new vapor tensions reported). The latter process required heat and gave only a 43% yield, suggesting complications if  $\text{ICN}$  is used to open  $(\text{CF}_3\text{P})_n$  rings into chain polyphosphines. The reaction of  $(\text{CF}_3)_2\text{PCN}$  with diborane gives a yellow viscous liquid adduct formulated as  $(\text{CF}_3)_2\text{PCN}\cdot\text{BH}_3$ . More extensive reaction leads to some formation of  $(\text{CF}_3)_2\text{PH}$  and  $\text{P}_2(\text{CF}_3)_4$ ; and heating leads to non-volatile plastic material which seems to develop chemical resistance as the temperature is raised.

An exploratory experiment has produced a volatile compound purporting to be  $\text{CF}_3\text{P}(\text{CN})_2$ .



VI. List of References for Appendix I

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12. F. W. Bennett, H. J. Emeléus, and R. N. Haszeldine, J. Chem. Soc., 1953, 1570.







## APPENDIX II. NEW COMPOUNDS

Listed in Table XXXII are the new compounds prepared during the year 1961 under Air Force Contract No. AF 33(616)-7810. References indicate page numbers of WADC Technical Report 57-126, Part VI.



TABLE XXXII

New Compounds

Name	Formula
<u>PHOSPHINES</u>	
Bis(trifluoromethyl)trifluoroacetonylphosphine	$(\text{CF}_3)_2\text{POCCF}_3$
Dineopentylphosphine	$(\text{neo-C}_5\text{H}_{11})_2\text{PH}$
Neopentylphenylphosphine	$\text{neo-C}_5\text{H}_{11}(\text{C}_6\text{H}_5)\text{PH}$
Methyl- $\beta$ -hydroxyethylphosphine	$\text{HOCH}_2\text{CH}_2(\text{CH}_3)\text{PH}$
Dineopentylchlorophosphine	$(\text{neo-C}_5\text{H}_{11})_2\text{PCl}$
Neopentylphenylchlorophosphine	$\text{neo-C}_5\text{H}_{11}(\text{C}_6\text{H}_5)\text{PCl}$
Methyl(3-dimethylaminopropyl)phosphine	$(\text{CH}_3)_2\text{N}(\text{CH}_2)_3\text{PHCH}_3$
Dimethylaminodineopentylphosphine	$(\text{CH}_3)_2\text{NP}(\text{neo-C}_5\text{H}_{11})_2$
Dimethylaminoneopentylphenylphosphine	$(\text{CH}_3)_2\text{NP}(\text{neo-C}_5\text{H}_{11})(\text{C}_6\text{H}_5)$
p-Bis(methyldimethylaminophosphino)-benzene	$p\text{-C}_6\text{H}_4[\text{P}(\text{CH}_3)\text{N}(\text{CH}_3)_2]_2$
<u>POLYPHOSPHINES</u>	
sym-Dineopentylldiphenylbiphosphine	$[(\text{neo-C}_5\text{H}_{11})(\text{C}_6\text{H}_5)\text{P}]_2$
Pentakis(trifluoromethyl)-triposphine	$(\text{CF}_3)_2\text{PP}(\text{CF}_3)\text{P}(\text{CF}_3)_2$
1,2,3,4-Tetrakis(trifluoromethyl)-tetraphosphine	$\text{CF}_3(\text{H})\text{P}(\text{PCF}_3)_2\text{P}(\text{H})\text{CF}_3$
<u>PHOSPHINE BORINES</u>	
Methyltrifluoromethylphosphine borine	$\text{CH}_3(\text{CF}_3)\text{PH}:\text{BH}_3$
Dineopentylphosphine borine	$(\text{neo-C}_5\text{H}_{11})_2\text{PH}:\text{BH}_3$



M.p., °C.	B.p., °C./mm.	Remarks
—	0/58	Unstable liquid
—	60.5-62.0/10	
—	94-95/10	
—	67/20	
—	55.0-55.5/3	
—	110-113/10	
—	64-67/29-30	
—	63-70/5.5-6.0	
—	118-121/11	
—	95-130/10 <sup>-4</sup>	Crude Material
—	—	
—	133	Somewhat unstable
—	—	Very unstable liquid
< -78	22°/17.5	
55.5-57.0	—	



Name	Formula
Neopentylphenylphosphine borine	$(\text{neo-C}_5\text{H}_{11})(\text{C}_6\text{H}_5)\text{PH}:\text{BH}_3$
Methyl(3-dimethylaminopropyl)phosphine bis(borine)	$\text{H}_3\text{B}:(\text{CH}_3)_2\text{N}(\text{CH}_2)_3\text{PHCH}_3:\text{BH}_3$
<u>TRIBOROPHANES</u>	
P-Hexamethyltriborophane-B-d <sub>6</sub>	$[(\text{CH}_3)_2\text{PBD}_2]_3$
1,3,5-Trimethyl-1,3,5-tris-(trifluoromethyl)triborophane	$[\text{CH}_3(\text{CF}_3)\text{PBH}_2]_3$
P-Hexakis(trifluoromethyl)-triborophane-B-d <sub>6</sub>	$[(\text{CF}_3)_2\text{PBD}_2]_3$
1,3,5-Trimethyl-1,3,5-triallyl-triborophane	$[\text{CH}_3(\text{CH}_2=\text{CHCH}_2)\text{PBH}_2]_3$
1,3,5-Trimethyl-1,3,5-tripropyl-triborophane	$[\text{CH}_3(\text{C}_3\text{H}_7)\text{PBH}_2]_3$
1,3,5-Trimethyl-1,3,5-tributyl-triborophane	$[\text{CH}_3(\text{C}_4\text{H}_9)\text{PBH}_2]_3$
1,3,5-Trimethyl-1,3,5-triamyl-triborophane	$[\text{CH}_3(\text{C}_5\text{H}_{11})\text{PBH}_2]_3$
1,3,5-Trimethyl-1,3,5-trihexyl-triborophane	$[\text{CH}_3(\text{C}_6\text{H}_{13})\text{PBH}_2]_3$
1,3,5-Trimethyl-1,3,5-triheptyl-triborophane	$[\text{CH}_3(\text{C}_7\text{H}_{15})\text{PBH}_2]_3$
1,3,5-Trimethyl-1,3,5-trioctyl-triborophane	$[\text{CH}_3(\text{C}_8\text{H}_{17})\text{PBH}_2]_3$
P-Hexaneopentyltriborophane	$[(\text{neo-C}_5\text{H}_{11})_2\text{PBH}_2]_3$



M.p., °C.	B.p., °C./mm.	Remarks
28-29	—	
57.2-59.2	—	
—	—	IR spectrum
Near ambient	—	
—	—	IR spectrum
—	—	Liquid
—	—	Liquid
—	—	Liquid
—	—	Liquid
—	—	Liquid
—	—	Liquid
-52	—	Liquid
201.5-206.0	—	



Name	Formula
1,3,5-Trimethyl-1,3,5-triphenyl-triborophane	$[\text{CH}_3(\text{C}_6\text{H}_5)\text{PBH}_2]_3$
1,3,5-Trineopentyl-1,3,5-triphenyl-triborophane	$[\text{neo-C}_5\text{H}_{11}(\text{C}_6\text{H}_5)\text{PBH}_2]_3$
1,3,5-Trimethyl-1,3,5-tris-(3-dimethylaminopropyl)triborophane	$[(\text{CH}_3)_2\text{N}(\text{CH}_2)_3(\text{CH}_3)\text{PBH}_2]_3$
P-Hexamethyl-B,B',B''-trichloro-triborophane	$[(\text{CH}_3)_2\text{PBHCl}]_3$
P-Hexamethyl-B,B,B',B''-tetrachloro-triborophane	$[(\text{CH}_3)_2\text{PBHCl}]_2[(\text{CH}_3)_2\text{PBCl}_2]$
P-Hexamethyl-B-pentachloro-triborophane	$[(\text{CH}_3)_2\text{PBCl}_2]_2[(\text{CH}_3)_2\text{PBHCl}]$
P-Hexamethyl-B,B,B',B''-tetrabromo-triborophane	$[(\text{CH}_3)_2\text{PBHBr}]_2[(\text{CH}_3)_2\text{PBr}_2]$
P-Hexamethyl-B,B'-diiodotriborophane	$[(\text{CH}_3)_2\text{PBHI}]_2[(\text{CH}_3)_2\text{PBH}_2]$
P-Hexamethyl-B-ethyltriborophane	$[(\text{CH}_3)_2\text{PBH}_2]_2[(\text{CH}_3)_2\text{PBHC}_2\text{H}_5]$
P-Hexamethyl-B-pentamethyltriborophane	$[(\text{CH}_3)_2\text{PB}(\text{CH}_3)_2]_2[(\text{CH}_3)_2\text{PBHCH}_3]$
P-Hexamethyl-B-formoxytriborophane	$[(\text{CH}_3)_2\text{PBH}_2]_2[(\text{CH}_3)_2\text{PBHOOC}]$
P-Hexamethyl-B-acetoxytriborophane	$[(\text{CH}_3)_2\text{PBH}_2]_2[(\text{CH}_3)_2\text{PBHOOCCH}_3]$
P-Hexamethyl-B-benzoytriborophane	$[(\text{CH}_3)_2\text{PBH}_2]_2[(\text{CH}_3)_2\text{PBHOOC}_6\text{H}_5]$
P-Hexamethyl-B-isocyanatotriborophane	$[(\text{CH}_3)_2\text{PBH}_2]_2[(\text{CH}_3)_2\text{PBHNCO}]$
P-Hexamethyl-B-(3,3-diethylureido)-triborophane	$[(\text{CH}_3)_2\text{PBH}_2]_2[(\text{CH}_3)_2\text{PBHNHCON}(\text{C}_2\text{H}_5)_2]$
P-Hexamethyl-B-thiocyanotriborophane	$[(\text{CH}_3)_2\text{PBH}_2]_2[(\text{CH}_3)_2\text{PBHSCN}]$
P-Hexamethyl-B-mercaptotriborophane	$[(\text{CH}_3)_2\text{PBH}_2]_2[(\text{CH}_3)_2\text{PBHS}]$



M.p., °C.	B.p., °C./mm.	Remarks
124-126 79-81	—	Stereoisomers
188-191 100-104	—	Stereoisomers
—	—	Liquid
—	—	Solid
—	—	Solid
—	—	Solid
208-209	—	
118.5-119.5	—	
36.5-37.0	—	
—	—	Solid
45.5-46.5	—	
44-45	—	
81.0-81.5	—	
71-72	—	
101-102	—	
63-64	—	
51-52	—	



Name	Formula
P-Hexamethyl-B-methanethio-triborophorane	$[(CH_3)_2PBH_2]_2[(CH_3)_2PBHSCH_3]$
<u>POLYCYCLIC BOROPHANE POLYMERS</u>	
P-Nonamethyl-B-bromobicyclo[4.4.0]-pentaborophane	$[(CH_3)_2PBH_2]_3[(CH_3)_2PBHBr]CH_3PBH$
<u>LINEAR POLYBOROPHANES</u>	
P-Methylbutylborophane polymer	$[CH_3(C_4H_9)PBH_2]_x$
P-Methylamylborophane polymer	$[CH_3(C_5H_{11})PBH_2]_x$
P-Methylhexylborophane polymer	$[CH_3(C_6H_{13})PBH_2]_x$
P-Methylheptylborophane polymer	$[CH_3(C_7H_{15})PBH_2]_x$
P-Methyloctylborophane polymer	$[CH_3(C_8H_{17})PBH_2]_x$
P-(3,3-dimethylcyclotrimethylene)-borophane polymer	$[(CH_3)_2C(CH_2)_2PBH_2]_x$
P-Cyclotetramethyleneborophane polymer	$[CH_2(CH_2)_3PBH_2]_x$
<u>MISCELLANEOUS PHOSPHORUS COMPOUNDS</u>	
Trifluoromethylphosphinic acid dimer	$(CF_3HPOOH)_2$
Benzene-1,4-bis(methylphosphinic acid)	$p-C_6H_4[P(CH_3)OOH]_2$
Dimethylaminophenylphosphonyl chloride	$C_6H_5[(CH_3)_2N]POCl$
Diphenylphosponamide	$(C_6H_5)_2PONH_2$
Diphenylphosphonyl azide	$(C_6H_5)_2PON_3$
Diphenylthiophosphonyl azide	$(C_6H_5)_2PSN_3$



M.p., °C.	B.p., °C./mm.	Remarks
60-61		
143-144 123.5-125.0	—	Isomers
—	—	Viscous liquid
—	—	Viscous liquid
—	—	Viscous liquid
—	—	Viscous liquid
—	—	Viscous liquid
—	—	Glass
—	—	Glass
—	214(calc.)	Corrects $[\text{CF}_3\text{P}(\text{OH})_2]_2$ WADC TR 57-126, Pt V, p. 228
231-236	—	
—	102-103/0.3	$n_D^{20}$ 1.5472
154-155	—	
—	137-140/0.05	$n_D^{20}$ 1.6077
—	—	Turns red on distillation at $10^{-5}$ mm.

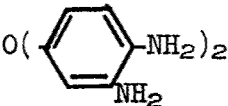


Name	Formula
Bis( <u>p</u> -chlorophenyl)phosphonyl azide	$(\underline{p}\text{-ClC}_6\text{H}_4)_2\text{PON}_3$
Bis( <u>p</u> -tolyl)phosphonyl azide	$(\underline{p}\text{-CH}_3\text{C}_6\text{H}_4)_2\text{PON}_3$
Diphenylthiophosphonimidotriphenylphosphorane	$(\text{C}_6\text{H}_5)_2\text{P(S)N=P(C}_6\text{H}_5)_3$
Diphenylphosphonimidophenyldimethylphosphorane	$(\text{C}_6\text{H}_5)_2\text{P(O)N=P(CH}_3)_2\text{C}_6\text{H}_5$
Diphenylphosphonimidotris( <u>p</u> -tolyl)phosphorane	$(\text{C}_6\text{H}_5)_2\text{P(O)N=P}(\underline{p}\text{-CH}_3\text{C}_6\text{H}_4)_3$
Bis( <u>p</u> -chlorophenyl)phosphonimido-triphenylphosphorane	$(\underline{p}\text{-ClC}_6\text{H}_4)_2\text{P(O)N=P(C}_6\text{H}_5)_3$
Bis( <u>p</u> -tolyl)phosphonimidotriphenylphosphorane	$(\underline{p}\text{-CH}_3\text{C}_6\text{H}_4)_2\text{P(O)N=P(C}_6\text{H}_5)_3$
Bis(triphenylphosphoraneimino)-diphenylsilane	$(\text{C}_6\text{H}_5)_2\text{Si[N=P(C}_6\text{H}_5)_3]_2$
<u>MISCELLANEOUS COMPOUNDS</u>	
4,4'-Diacetylamino-diphenyl ether	$\text{O}(\text{C}_6\text{H}_4\text{-NHCOCH}_3)_2$
3,3'-Dinitro-4,4'-diacetylamino-diphenyl ether	$\text{O}(\text{C}_6\text{H}_3(\text{NO}_2)_2\text{-NHCOCH}_3)_2$
3,3'-Diamino-4,4'-diacetylamino-diphenyl ether	$\text{O}(\text{C}_6\text{H}_3(\text{NH}_2)_2\text{-NHCOCH}_3)_2$
3,3',4,4'-Tetraacetylamino-diphenyl ether	$\text{O}(\text{C}_6\text{H}_2(\text{NHCOCH}_3)_4)_2$
3,3'-Dinitro-4,4'-diaminodiphenyl ether	$\text{O}(\text{C}_6\text{H}_3(\text{NO}_2)_2\text{-NH}_2)_2$



M.p., °C.	B.p., °C./mm.	Remarks
—	—	$n_D^{20}$ 1.6246
—	—	Distills at $10^{-5}$ mm.
179.0-179.5	—	Distills at $10^{-5}$ mm.
155-157	—	Solid at $-78^{\circ}\text{C}$ .
135-140	—	
205-208	—	
176-178	—	
—	—	Solid
225-227	—	
215.0-215.5	—	Yellow
213-214	—	
222-226	—	
178.5-179.0	—	Red



Name	Formula
3,3',4,4'-Tetraaminodiphenyl ether	$O(\text{C}_6\text{H}_3\text{NH}_2)_2$ 
Polymer from Benzene-1,4-diboronic acid and 3,3',4,4'-Tetraaminodiphenyl ether	$[\text{C}_6\text{H}_4\text{B}(\text{NH})_2\text{C}_6\text{H}_3\text{OC}_6\text{H}_3(\text{NH})_2\text{B}]_x$



M.p., °C.	B.p., °C./mm.	Remarks
120-122	—	Darkens rapidly
> 375	—	



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